

Personal power systems

Derek Dunn-Rankin ^{a,*}, Elisângela Martins Leal ^a, David C. Walther ^b

^a Mechanical and Aerospace Engineering Department, University of California, Irvine, CA 92697, USA

^b Berkeley Sensor and Actuator Center, University of California, Berkeley, CA 94720-1774, USA

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Abstract

The lack of compact, efficient, human compatible, lightweight power sources impedes the realization of machine-enhanced human endeavor. Electronic and communication devices, as well as mobile robotic devices, need new power sources that will allow them to operate autonomously for periods of hours. In this work, a personal power system implies an application of interest to an individual person. The human-compatible gravimetric energy density spans the range from 500 to 5000 Wh/kg, with gravimetric power density requirements from 10 to 1000 W/kg. These requirements are the primary goals for the systems presented here. The review examines the interesting and promising concepts in electrochemical, thermochemical, and biochemical approaches to small-scale power, as well as their technological and physical challenges and limitations. Often it is the limitations that dominate, so that while the technology to create personal autonomy for communications, information processing and mobility has accelerated, similar breakthroughs for the systems powering these devices have not yet occurred.

Fuel cells, model airplane engines, and hummingbird metabolism, are three promising examples, respectively, of electrochemical, thermochemical, and biochemical power production strategies that are close to achieving personal power systems' power demands. Fuel cells show great promise as an energy source when relatively low power density is demanded, but they cannot yet deliver high peak powers nor respond quickly to variable loads. Current small-scale engines, while achieving extraordinary power densities, are too inefficient to achieve the energy density needed for long-duration autonomous operation. Metabolic processes of flying insects and hummingbirds are remarkable biological energy converters, but duplicating, accelerating, and harnessing such power for mobility applications is virtually unexplored. These challenges are significant, and they provide a fertile environment for research and development.

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Contents

1. Introduction	423
1.1. Need for personal power systems	423
1.2. Scaling discussion	426

* Corresponding author. Tel.: +1 949 824 8745; fax: +1 949 824 8585.

E-mail address: ddunnran@uci.edu (D. Dunn-Rankin).

1.3.	Matching power demand with power source characteristics	428
2.	Personal power generation	430
2.1.	Energy release and power extraction	430
2.2.	Summary	432
3.	Electrochemical personal power	432
3.1.	Batteries	434
3.1.1.	Lithium batteries	435
3.1.2.	Advances in component technologies	436
3.1.3.	Nickel-metal hydride (NiMH) batteries	437
3.1.4.	Summary	438
3.2.	Fuel cells	438
3.2.1.	Proton exchange membrane fuel cell (PEMFC)	440
3.2.2.	Direct methanol fuel cell (DMFC)	440
3.2.3.	Direct formic acid fuel cells (DFAFC)	441
3.2.4.	Other fuel cell systems for personal power	442
3.2.5.	Summary	443
3.3.	Conclusions	443
4.	Thermochemical personal power	443
4.1.	Combustion issues	444
4.1.1.	Flame quenching	444
4.1.2.	Turbulence	445
4.1.3.	Friction	446
4.1.4.	Fuel issues	447
4.2.	Fueling comparison between thermochemical power and electrochemical power	447
4.2.1.	Distributed power	448
4.3.	Survey of personal power engines	448
4.3.1.	Static systems	448
4.3.2.	Dynamic systems	449
4.4.	Turbomachinery approaches	451
4.5.	Internal combustion engine approaches	451
4.6.	Conclusions	455
5.	Biochemical personal power	455
5.1.	Biochemical energy efficiency	456
5.2.	Control of power generation	457
5.3.	Power for animal flight	458
5.4.	Biochemical heat generation	458
5.5.	Summary and conclusions	459
6.	Personal power summary and concluding remarks	459
	Acknowledgements	459
	References	460

1. Introduction

1.1. Need for personal power systems

The opportunities and demand for devices that enhance autonomous human mobility, monitoring, and communication is growing rapidly, and power sources to energize these mobile systems are or will be critical to meeting this demand. Fig. 1 illustrates some of the advanced devices existing or soon to be offered for human mobility enhancement. Unfortunately, the systems available for powering these devices are not equally advanced. Personal autonomy through portable

networks, computation and communication, hand-held or hand-launched robotic devices, artificial organs, and exoskeletal systems requires compact, efficient, human-compatible power sources. Consequently, there is a looming need for revolutionary technologies that produce high power densities in packages that are compatible with human use. As shown in Fig. 1, the devices must be implantable in some cases, placing further constraints on the power system. To meet the desired requirements of these projected applications, new power systems need to achieve 10–100 times the power-to-weight performance of the current state-of-the-art human compatible power sources.

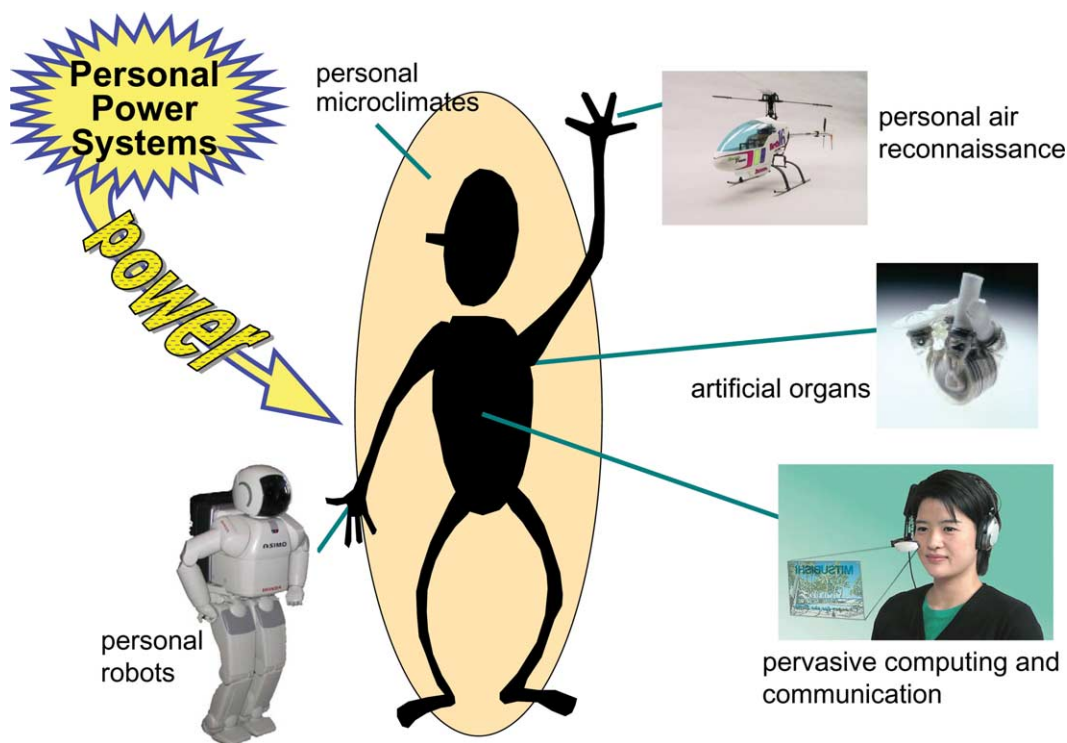


Fig. 1. Autonomous technologies needing new power sources.

These improvements will enable the user to perform tasks in a manner compatible with current physiological practice. Electronic devices for example could operate over the 10 working hours of the user rather than requiring an hourly recharge 10 times per workday.

The need for new personal power system technology to mobilize autonomy is often under-appreciated. Table 1 lists some examples of new or proposed personal mobility applications, their current power source performance, and the capabilities that a new power source would ideally provide. The table includes gravimetric power density based on power source mass (including fuel), but the volumetric gravimetric power density is also important to maintain portability. In addition to the obvious applications relevant to national security (e.g. air reconnaissance micro-vehicles,

networked soldiers of the future), market studies indicate a large civilian potential for small power systems, even those with relatively modest performance improvement over current batteries. The rechargeable battery market is approximately \$6 billion annually, and disposables (ending up in landfills primarily) contribute another \$31 billion [1]. Though not all of these batteries are powering systems that would be mobilized by new personal power strategies, the portable power supply market is projected to increase 7.2% per year through 2005, to \$10.7 billion [2]. These estimates are based on applications currently on the market, including laptop computers and wireless information exchange devices.

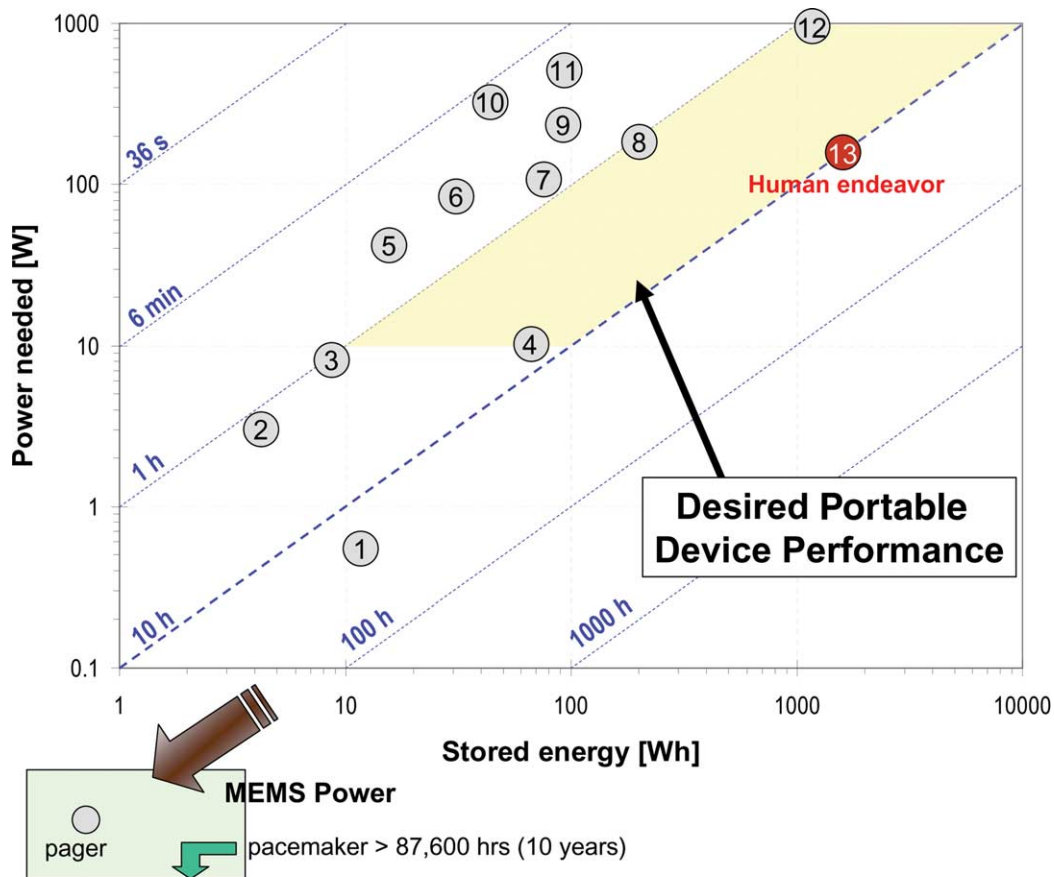
Artificial organs, though not currently a large market, represent a challenging application for

Table 1
Sample needs for personal power

Application	Power needs (W)	Typical current operating duration	Desired operating duration (h)	Power source goal
Artificial heart	30	0.5 h	10	300 Wh in 100 g mass
Humanoid robot	1000	15 min	5	5000 Wh in 5 kg or less
Exoskeleton	200	30 min	10	2000 Wh in 1 kg or less
Personal transport	1000	1 h	10	10,000 Wh in 5 kg or less
Augmented reality	200	1 h	10	2000 Wh in 1 kg or less

autonomous power and mobility because both the power levels are substantial and the devices must maintain biocompatibility. Similarly, exoskeletons for rehabilitation following neurologic injuries could be enabled by adequate power technology [3]. There are more than 700,000 new stroke victims annually, with 80% of them suffering severe ambulatory or manipulative function loss. More than two million people with stroke-induced chronic movement impairment are alive in the US today, and this number is likely to increase due to the graying of the population and improving survival rates. In addition, more than 10,000 Americans experience a spinal cord injury (SCI) each

year, joining the 200,000 individuals with an existing SCI. Currently, SCI rehabilitation is accomplished manually, with three physiotherapists typically required to carry the patient's limbs through the appropriate motions. Robotic devices have been attempted (e.g. [4]), but none of them are mobile. Robotic mobility requires substantial absolute power levels and portable robots demand high power densities as well. In addition to mobile rehabilitation, other nascent product markets are bottlenecked by a lack of effective power sources. Portable augmented reality [5] and personal transporters, such as the Segway [6], are examples. Finally, personal power can energize microclimate suits for



- | | |
|-----------------------------|------------------------------|
| 1 Bock C-Leg active knee | 7 Personal microclimate |
| 2 Cell phone | 8 UAV-Pointer |
| 3 4G cell phone | 9 Exoskeleton |
| 4 Minimal wearable computer | 10 Micro aircraft |
| 5 Artificial heart | 11 Honda humanoid robot |
| 6 Small personal robot | 12 Segway personal transport |

Fig. 2. Personal mobility applications listed in Table 1.

extreme weather conditions, as well as search and rescue operations that use autonomous mobile robots to explore potentially hazardous environments, or to canvass regions of open sea or land.

As shown in Fig. 2 the personal mobility applications listed in Table 1 (along with others) require power levels ranging from 10 to 1000 W, and they currently operate for an hour or less on their available power sources. In order to be compatible with human function, however, desirable devices should perform more on the order of 10 h at these power levels, with no change in system size. It is important to recognize that the absolute power range needed for enhanced human autonomy far exceeds the microwatt levels needed by sensors, MEMS devices, pagers, and pacemakers. Thus, many of the strategies envisioned for powering these tiny systems (e.g. ambient motion power harvesting [7], micro fuel cells [8], and biomolecular motors [9]) may never be sufficient for personal power systems. Fig. 3 puts in perspective the personal power level relative to electromechanical devices and biological systems. On this scale, personal power spans the range from bats to horses.

1.2. Scaling discussion

Although not necessarily microscale systems, personal power devices nevertheless need to be relatively small, having length scales in the range from 1 mm to 10 cm. The entire system volume (including fuel storage) should range from 5 ml to 5 l, with mass from 5 g to 5 kg. Fig. 4 illustrates graphically the desired physical size of personal power systems for 10-h operation at 10, 100, and 1000 W, along with the equivalent size of a current battery solution for the 100 W option. These personal power graphics intend to represent the entire power system, including fuel and any power conversion hardware necessary. This scaling means that human-compatible gravimetric energy

- 10000 W – riding lawnmower ~ elephant

- 1000 W – microwave oven ~ horse
- 100 W – light bulb ~ human
- 10 W – small laptop ~ bat

Personal Power

- 1 W – cell phone ~ hummingbird
- 10 mW – pager ~ blowfly
- 10 μ W – pacemaker ~ fruit fly

Fig. 3. Perspective of personal power level relative to electro-mechanical devices and biological systems.

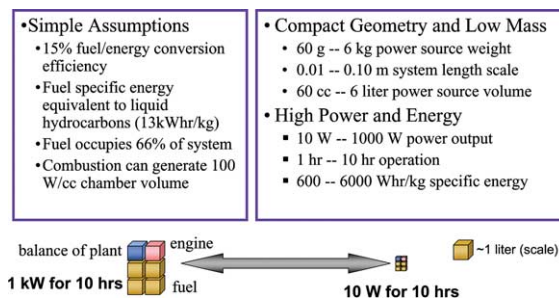


Fig. 4. Desired physical size of personal power systems.

density spans the range from 500 to 5000 Wh/kg, with gravimetric power density requirements from 10 to 1000 W/kg. In this work, personal power implies an application of interest to an individual person, rather than an explicit power, volume, or mass range. As such, it covers power generation that encompasses previously defined regimes including, but not limited to, ‘palm-power’, meso-scale power, small-scale, micropower generation (MPG), etc. Several recent reviews have been published to address the issues of scaling as well as challenges associated with micropower generation [10–12], but they do not discuss in detail the range presented in this paper.

A very useful graphical technique for comparing various personal power devices is the Ragone plot. Ragone originated this plot in a paper at the May 1968 meeting of the Society of Automotive Engineers, where the first examples were shown [13]. The diagram is a log–log plot, which allows a significant spectrum of gravimetric power density (kW/kg) and gravimetric energy densities (kWh/kg) to be plotted compactly. Fig. 5 shows a Ragone plot, with the personal power range shaded. As in Fig. 2, the diagonal lines indicate operating duration. Each of the current power provision technologies is represented by a curve on the Ragone plot since there is generally a relationship between gravimetric power density and gravimetric energy density. With batteries and fuel cells, for example, as the system power increases, less energy can be extracted. The highest gravimetric energy density batteries can only provide miniscule levels of power. The approximately horizontal lines represent a fixed power converter mass with increasing fuel mass when the fuel is a small fraction of the total. The roll-off for engines occurs as the mass of fuel begins to dominate the mass of the engine. Eventually, the gravimetric energy density is controlled by the engine efficiency and energy content of the fuel, leading ultimately to a vertical asymptote as the total mass increases with no increase in power. Elastic elements and ultra-capacitors

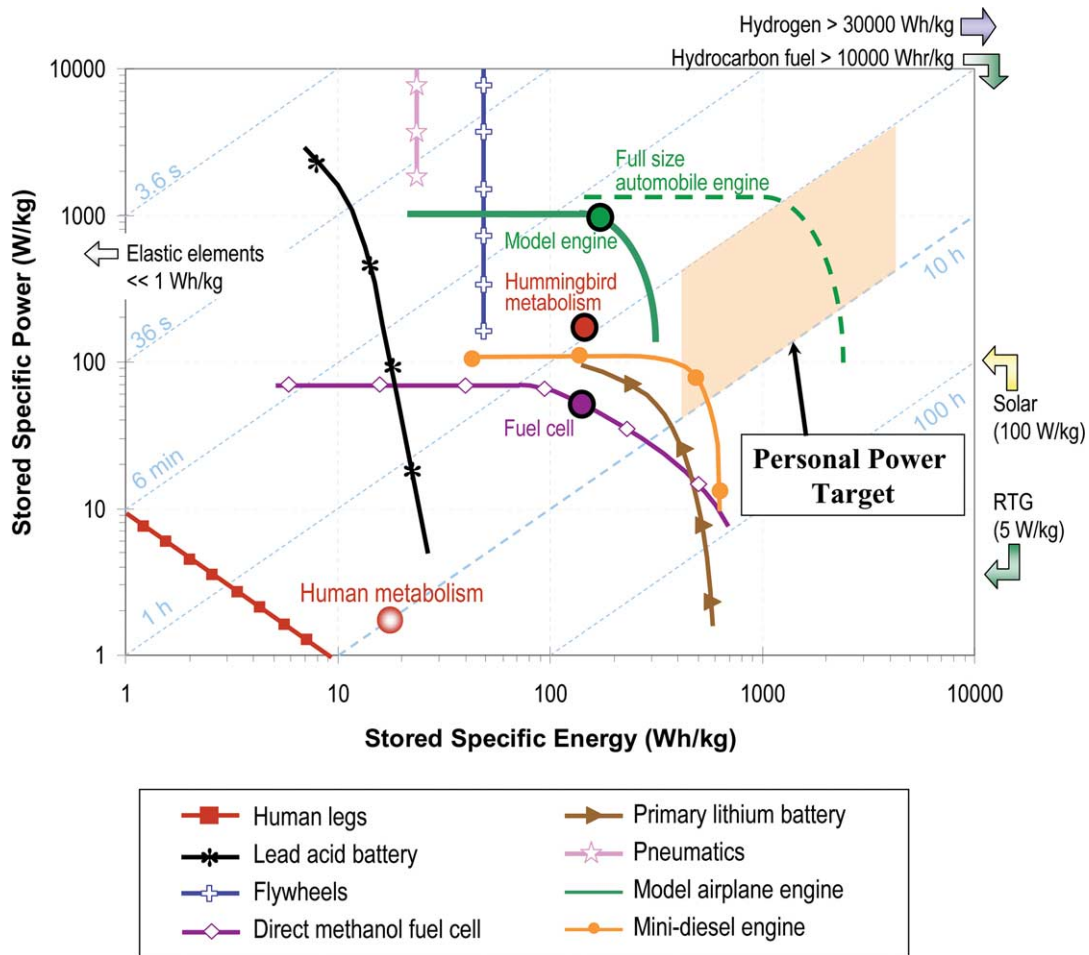


Fig. 5. Ragone plot of existing power systems.

have enormous power densities since all of their stored energy can be released in a very short time, but these devices have poor energy storage capabilities on a mass basis. Existing rechargeable batteries cannot yet achieve the gravimetric energy density and gravimetric power density required for autonomous personal power. Typical human metabolism has moderate gravimetric energy density but gravimetric power density in the range of only a few W/kg, so, as mentioned above, energy harvesting from body functions alone cannot ever achieve personal power target performance. Fig. 5 is based on existing small-scale power systems, not laboratory devices, and it is intended to give the basic ranges of performance. Individual systems may have behavior that is slightly different, but the general levels are representative.

Although current power source technologies do not meet personal power demands, there are fuels available with clearly sufficient inherent gravimetric energy

density if that energy can be released quickly and efficiently. Formic acid, ammonia, and methanol are being considered among the most promising liquid fuel options for low temperature fuel cells. Based on their lower heating values (LHV), these fuels have energy densities of 1.6, 5.2, and 5.6 kWh/kg, respectively. Liquid hydrocarbon fuels have gravimetric energy density on the order of 13 kWh/kg, which with 25% conversion efficiency would provide close to 3.25 kWh/kg, a value near the upper end of the desired personal power range. This high gravimetric energy density is the oft-stated reason for exploring combustion as a superior power source to batteries at small-scales [13]. This is not a fair comparison, however, as only the fuel is considered in one case (hydrocarbons) and the entire power generator in the other (battery). If lithium alone were examined as the active ion species in the battery, its gravimetric energy density would be 13.5 kWh/kg (calculated assuming an electrochemical

process which liberates one electron per Li atom and moves it across a 3.5 V potential, i.e. the voltage of a Li metal battery). This gravimetric energy density is comparable to that of hydrocarbons. Even if the cathode–anode matrix that stores lithium in current commercial formulations were used, the gravimetric energy density (of what is essentially the battery and fuel tank) would be 1.6 kWh/kg, which is again quite substantial. Therefore the entire power system should be evaluated, including fuel, fuel storage and delivery, and power conversion. From this system's view, batteries remain a strong personal power option for many applications. Thermochemical systems are the clear choice for propulsion and power generation at the large scale because of their ability to achieve high efficiency and to further utilize the thermodynamic availability of the exhaust. In order for small-scale thermochemical devices to become viable candidates to supplant electrochemical systems, however, the balance of plant components must be minimized and the efficiency reasonably maintained as the scale is reduced to have superior gravimetric energy density to the best batteries. Recent advances in microfabrication are helping to address the balance of plant components.

On a gravimetric energy density basis, hydrogen appears an excellent candidate fuel (> 30 kWh/kg), but all storage strategies for hydrogen are currently excessively large or heavy or both on the personal power scale. Although there are some promising approaches for hydrogen storage on-board vehicles, Schlappbach and Züttel [14] and Podolski [15] show that volume and mass density of hydrogen storage at the levels necessary for personal power is nontrivial. Fig. 6 shows a comparison of hydrogen technologies in terms of gravimetric energy density and gravimetric power density (Fig. 6(a)) and storage per mass and per volume (Fig. 6(b)). The upper right portion of Fig. 6(b) is most desirable for mobile power applications. For example, in the ideal scenario of a 100 W, 50% efficient fuel cell operating on hydrogen and ambient air, 10 h of operation would require only 56 g of hydrogen. Unfortunately, 1.5 kg of typical hydride would also be needed to store this hydrogen. Hence, at least for the present, only two fuel sources can provide sufficient gravimetric energy density and power (on both a mass and volumetric basis) to reach the ultimate goals of personal power systems: radioactive materials and condensed fuels (e.g. liquid hydrocarbons). Nuclear sources continue to be contenders for extended space flight missions (e.g. the radioisotope thermoelectric generator indicated in the lower right corner of Fig. 5), but system engineering requirements make it difficult

for them to achieve high gravimetric power density, not to mention the issues associated with human compatibility [16]. There have also been some contemplations of nuclear-based batteries [17] and radioisotope power generators [18], but at the power scales targeted in this work, these are far from feasibility at the moment [17]. Liquid hydrocarbon fuel reactions, on the other hand, produce heat, carbon dioxide and water, the same pollutants that human metabolism generates, and storage of liquid fuels is not complicated. To date, however, extracting useful work from hydrocarbon fuels at the requisite personal power and energy densities has only been achieved in engines with length and mass scales many times those compatible with human comfort. Automobile engines, for example, can produce more than 1 kW/kg and allow energy storage density of 2 kWh/kg. Unfortunately, even the M54 magnesium/aluminum composite engines, the lightest in their class, are unacceptably heavy and bulky for portable human use [19].

1.3. Matching power demand with power source characteristics

In addition to the curves showing gravimetric power/energy density tradeoffs, Fig. 5 indicates three promising example power sources (circled in black) close to achieving PPS power demands: model airplane engines, hummingbird metabolism, and fuel cells. These three points are at the knee of what would be their Ragone curves, and they motivate, respectively, thermochemical, biochemical, and electrochemical power production strategies that could be developed and hybridized to provide personal power. Though some of these strategies have been, and continue to be, examined (e.g. [13,20–25]), reaching the requisite gravimetric power density and gravimetric energy density goals still requires a substantial interdisciplinary research and development effort. Current engines, for example, while achieving extraordinary power densities, are too inefficient to meet the gravimetric energy density goals of personal power or even those established by the DARPA Palm Power Program [26]. Metabolic processes of flying insects and hummingbirds are remarkable biological energy converters, but duplicating and harnessing such power for mobility applications is virtually unexplored. Fuel cells show great promise as an electrical energy source, but they cannot yet deliver high peak powers nor respond quickly to variable loads. It is possible that hybrids among these generic technologies might produce further gains. Fig. 7 describes the situation graphically;

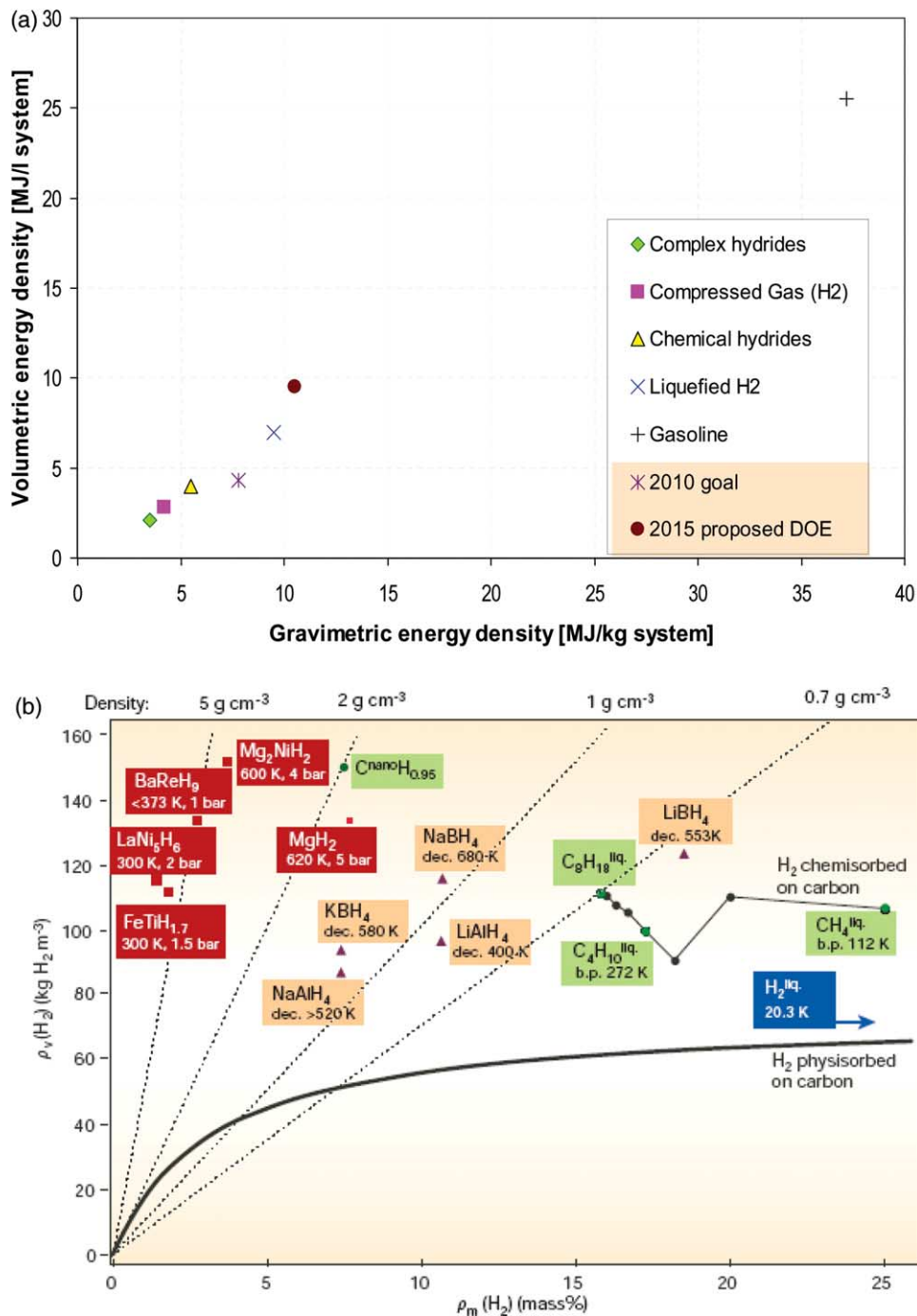


Fig. 6. Comparison of hydrogen technologies in terms of: (a) gravimetric energy density and gravimetric power density [15] and (b) stored hydrogen per mass and per volume [14]. Used with permission.

in order to meet autonomous functional demands, electrochemical power sources need to improve in gravimetric energy density and gravimetric power density, thermochemical systems need to improve in

efficiency, and biochemical approaches need to improve on the best systems found in nature. Hybrid designs will likely be necessary to take these improvements to their final step. The goal of this

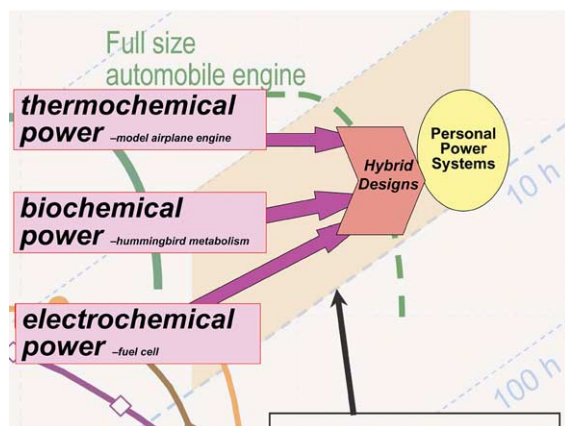


Fig. 7. Personal power conceptual goal.

review, therefore, is not so much to describe personal power solutions, but rather to discuss some of the issues, concepts, possibilities, and opportunities that are related to these basic power generation strategies, or their hybrids, in order to speculate on the potential for next generation personal power systems.

2. Personal power generation

Fig. 8 defines the essence of any personal power system that takes in fuel, produces usable work or heat, and then exhausts products. Personal power requires high gravimetric energy density fuel, and the fuel processing step converts this fuel into a form that can be used by the energy extraction mechanism. Low temperature fuel cells, for example, might require sulfur removal or reforming of liquid hydrocarbons to hydrogen [27]. Energy release from high gravimetric energy density fuels can occur via biochemical, electrochemical, or thermochemical processes. Power extraction then converts the thermal, electrical, or mechanical energy released into the form needed by the application. Finally, exhaust management must maintain human compatibility with any exhaust products, including heat, noise, or chemical pollutants. Although

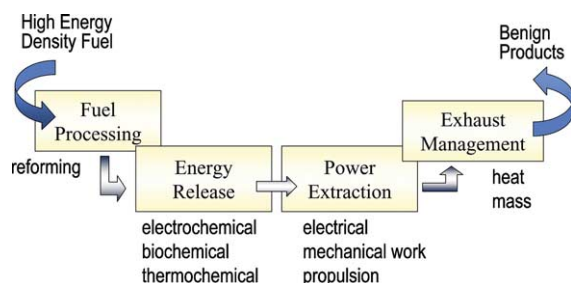


Fig. 8. Personal power generation science and technology.

this paper concentrates primarily on the middle two processes, it is often the fuel processing and exhaust management that dominate the system size and performance. In a direct methanol fuel cell (DMFC), for example, the fuel handling is a significant fraction of the overall device [28] and in butane fuel cell systems, the fuel reformation component is also significant [29].

2.1. Energy release and power extraction

Fig. 9 lists some examples of the key energy release and power extraction technologies that have been attempted for personal power use. Some are more popular than others, and for combustion, the principal activities have included all manner of engines. Power extraction, or the transduction of the energy released in the primary process to a form that accomplishes the task expected, ranges widely as well. The major markets currently perceived for personal power expect primarily an output of electrical energy [2]. If the energy release is in the form of heat, as with an engine, further steps are needed to generate electricity. Electrochemical energy release can be more direct, however, electrical power regulation is not always straightforward.

Fig. 10 shows the personal power system as a servant to the application it energizes. For example, the power profile demanded by the robotic or telecommunication system will dictate the required performance. Physically realizing any of the personal power strategies in functional devices requires precision manufacturing, often employing specifications and techniques that are at or beyond the practiced state-of-the-art. The power components must then be integrated into a compact power source or hybrid power system that meets the power profile requirements. Ideally, personal power system performance will, through system control, integration, and optimization, match the requested

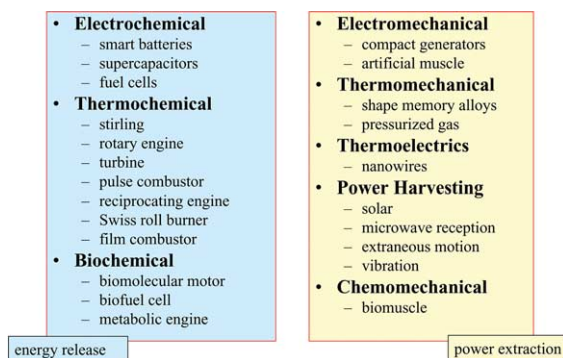


Fig. 9. Energy release and power extraction.

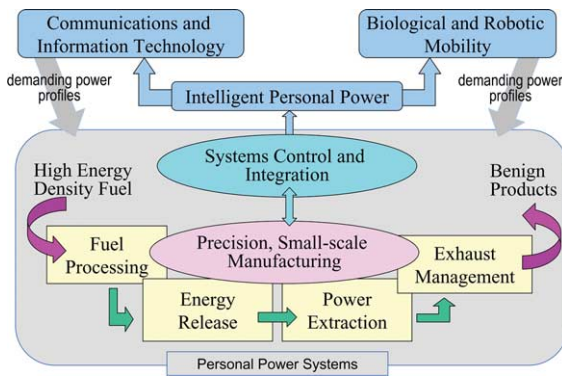


Fig. 10. Applications to define personal power systems.

power demand, as, for example, described by Maish [30].

To show the potential scope of personal power and to help give some concrete examples of personal power systems that would represent the kinds of improvements necessary to achieve the desired application objectives, the following paragraphs describe a few power system performance challenges. Three of the challenges reside within gravimetric power density technology areas and the remainder represents substantial systems integration efforts. The challenges include:

A. Intelligent electrochemical cell: batteries and fuel cells have reasonably good energy storage capabilities, but, due primarily to transport issues, they have difficulty meeting high personal power demands while maintaining high efficiency [31]. The challenge is to employ intelligent active feedback control, programmable electrical storage strategies, and novel electrochemical architectures to deliver 300 W (electrical) and 10-h operation in a 2 kg system package. To create an intelligent electrochemical cell will require sensors to monitor temperature and fuel, low power pumps and valves to control the fuel and air flows, the development of novel material constructs for fuel cells and fuel reforming, and high efficiency distributed energy storage devices compatible with electricity generation.

B. Biological power demonstration: this power challenge would use power sources modeled after the most energetic of hovering animals. The goal is to construct a biologically modeled system that can generate 30 W of electrical or mechanical work at 200 W/kg and 25% efficiency based on the energy content of the fuel. Two basic approaches are possible; one based entirely on biological organisms and the other mimicking metabolic behavior in an artificial

construct. To accomplish the goal requires an understanding of mitochondria behavior, replication, and survival in external environments, the creation of an artificial cell power system, fuel and oxygen delivery schemes, sensing and control for artificially regulating metabolism, power extraction strategies that may be thermal, chemical, or electrical, and the conversion of this power to mechanical or electrical energy.

C. Miniature high-efficiency engine: the concept is to develop an ultra-compact engine that maintains 20% fuel-to-mechanical conversion efficiency. The target is a 0.75 l and 0.5 kg engine capable of producing 1000 W of mechanical power. The design will likely entail a rotating shaft machine (such as an engine or small gas turbine). Thermal management of the engine to reduce heat losses, recovery of exhaust thermal energy through a secondary turbine, thermoelectric elements, or thermomechanical materials, and treatment of the exhaust gas stream for pollutant emission reduction will be required for consumer applications.

D. Personal electrical power module: the challenge is to develop an engine/generator set that can produce up to 1000 W of electrical power (W_e) for 4 h in a total package (fuel, engine, and exhaust treatment) smaller than 3 l, including the demonstration of the system.

E. Intermittent power module: this system is a compact and mobile energy source designed for high peak powers at short time intervals. This situation arises, for example, when powering joint motions, such as would be used for jumping robots [32] or for rehabilitating stroke patients [3]. The challenge is to construct a power module capable of 1 kW peak power, 2 Hz duty cycle, 2 h operation, and with 1 kg power system mass. These types of systems are currently designed to utilize combustion powered cylinders, including both monopropellant and air breathing systems. Other requirements include microscale liquid fuel control including valves, pumps, and potentially oxidizer pumps; high precision manufacturing of reaction chambers, pneumatic cylinders, actuators, and valves; liquid fuel combustion in small volumes, optimal control of pressure forces; and, eventually, noise suppression.

F. Biocompatible power module: this power source is intended for operation very close to or inside the human body. The goal is 100 W of electrical power for 10 h of continuous operation in a 0.5 kg package. To maintain biocompatibility it is important to control temperature and noise. This power source is targeted toward drug pumps, artificial organs, and personal electronics.

G. Power module for flight: maximum gravimetric power density is necessary for flight, and micro air vehicles are one of the most demanding applications for personal power. The goal for this module is a gravimetric power density higher than 400 W/kg and an energy storage density of greater than 3 kWh/kg.

These challenges represent examples of systems-level targets that illustrate a range of personal power profiles and the level of improvement needed to deliver power at the personal autonomous level. It is important to recognize that a common thread throughout these challenges is the need for auxiliary systems for sensing, actuation and control, in addition to the primary energy conversion components.

2.2. Summary

Fig. 5 shows the current state-of-the-art in personal power generation. Today's autonomy-enhancing devices, however, need more power than these sources can provide. Furthermore, the trajectory of power consumption in consumer products suggests that tomorrow's autonomous technologies will require even higher levels of gravimetric power density, gravimetric energy density, and adjustability. These needs are well recognized by all autonomous product developers, as they have all experienced the challenge of powering their devices. As an example, Intel has recently announced a working group consisting of representation from a dozen major computer and electronics companies (e.g. Microsoft, Dell Computers, Samsung) to identify the major issues preventing the 'all day laptop', a computer that operates for 8 h on a single charge [33]. Similarly, the Aerovironment Black Widow micro-air vehicle has a 30-min operating range [34], where the desire is a minimum of 2 h. The Portable Power Expo is now a yearly event, highlighting both new power sources and new methods for managing power to extend performance in personal electronic devices [35]. With such a clear commercial and technological demand for advanced power sources, it is not surprising that there has been substantial effort expended to meet it. This effort has led to steady, incremental improvements in battery performance, but not at the pace demanded by new power-hungry devices [36]. Recognizing this fact, the Defense Advanced Research Programs Agency (DARPA) has for some years supported development efforts for revolutionary compact power systems to enhance soldier mobility, efficacy, and communication [37–39]. Through this support, a variety of clever power generating devices were conceived. Microengines [13], heel strike power

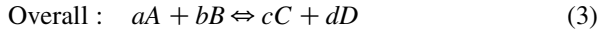
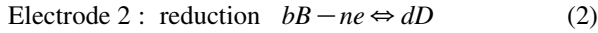
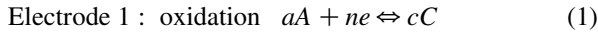
harvesting [40], and advanced thermoelectrics [41] are among these concepts. While some progress has been made, (see, for example, the gains in compact fuel cells [42]), the solution strategies have focused on single power technologies (e.g. fuel cells or engines) rather than comprehensive creation of hybrid power at the desired scale. In order to advance the technology further, studies should build on these early conceptual efforts and should bring an integrated approach to the development of hybrid personal power systems. To help put in context some of the design trade-offs needed for such hybrid design, the following sections describe the single technology concepts currently being explored for personal power use.

3. Electrochemical personal power

Electrochemical power generation is an incredibly diverse and sophisticated field, and several major academic and corporate concerns throughout the country and the world are trying to create the ultimate electrochemical power solution, with particular attention to the massive potential markets of electric or hybrid vehicles (i.e. 100 kW) and personal communication devices like cellular telephones (i.e. 3–5 W). The two principal foci of these efforts have been advanced lithium batteries [43,44] and fuel cells [45]. In both of these cases, power extraction from the electrochemical system is essentially transport limited (in anodes or cathodes or across electrolytes), and while electrochemical devices have achieved marginally sufficient gravimetric power density for vehicular applications, personal power demands at least a factor of 10 further improvement. Information on the basic fundamentals of batteries [46] and fuel cell systems [27,47,48] can be found in the literature. This review includes brief coverage of the fundamentals to help describe the performance of personal power electrochemical systems.

Batteries and fuel cells are electrochemical devices that convert chemical energy into electrical energy by electrochemical oxidation and reduction reactions, which occur at the electrodes [46]. The governing phenomena of electrochemical systems are essentially scale independent, and the basic physical structure of batteries and fuel cells is an electrolyte layer sandwiched by an anode (negative electrode) and cathode (positive electrode) on either side. The electrolyte provides ionic conduction, while the electrons generate power as they traverse an external circuit through the electrical load. In a cell, the reactions occur at the surfaces of the electrodes.

In generalized terms, the reaction at the electrodes and the overall reaction can be represented by, respectively [46]:



The change in the standard free energy, ΔG^0 , (i.e. the maximum electric energy that can be delivered by the chemicals that are stored within or supplied to the electrodes in the cell) of the reaction (3) is expressed as [46,47]:

$$\Delta G^0 = -n_e F E^0 \quad (4)$$

where F is the Faraday constant (96,487 C/mol), E^0 (V) is the standard potential at 0.101 MPa and 298 K and n_e is the number of participating electrons in the reaction. When the conditions are other than the standard state (0.101 MPa and 298 K), the voltage E_0 of a cell is given by the Nernst Eq. [49]:

$$E_0 = E^0 - \frac{RT}{n_e F} \ln \left[\frac{a_C^c a_D^d}{a_A^a a_B^b} \right] \quad (5)$$

where a_i is the activity of the relevant species. Chemical activity can be defined as the amount of a particular substance or ion, which is reactive where the reaction is occurring. A single ion activity is calculated by multiplying the concentration by the activity coefficient. In Eq. (5), R is the gas constant and T is the absolute temperature. In the case of a fuel cell, the maximum work available from a fuel source is also related to the free energy of reaction (ΔG_R), whereas the enthalpy of reaction (ΔH_R) is the pertinent quantity for a heat engine [27]:

$$\Delta G_R = \Delta H_R - T \Delta S_R \quad (6)$$

As shown in Eq. (6), the difference between ΔG_R and ΔH_R is proportional to temperature and to the change in entropy (ΔS_R).

Electrode reactions are characterized by both chemical and electrical changes and are heterogeneous in type. They may be as simple as the single step reduction of a metal or the overall process may be relatively complex, involving several steps. Before the electron transfer step, electroactive species must be transported to the electrode surface by migration or diffusion. The electroactive species needs to be adsorbed by the electroactive material either before the electron transfer step or after it. These behaviors

lead to losses and prevent some chemical energy from being converted to useful electric work during cell discharge. To determine actual cell performance, three losses must be subtracted from the Nernst potential: (1) activation polarization, (2) concentration polarization, and (3) ohmic polarization. When connected to an external load (R), the cell voltage V can be expressed as [46]:

$$V = E_0 - [\eta_{\text{act}} + \eta_{\text{conc}}]_{\text{anode}} - [\eta_{\text{act}} + \eta_{\text{conc}}]_{\text{cathode}} - iR_i \quad (7)$$

Where η_{act} and η_{conc} is the potential loss due to activation and concentration polarization, respectively; R_i is the internal resistance of the cell and i is the operating current. The Nernst equation characterizes the ability of the reactants to diffuse in the electrolyte from the bulk fluid flow and limits the current generation in the device. The activation polarization characterizes the energy needed to start the reaction. Activation losses are a function of the charge transfer kinetics of the electrochemical processes and are predominant at small current density. On the other hand, concentration polarization adjusts for the diffusion gradient into the active sites and is dominant when the cell is operating at high current density. Ohmic polarization is directly related to the internal resistance of the cell. It follows Ohm's law and describes the thermal losses caused by resistive heating that occur when a current passes through an electrolyte and through electrodes. For example, ideally a fuel cell can produce 1.23 V DC at ambient conditions while in practice its voltage output decreases with increasing discharge rate [46]. Results from Los Alamos National Laboratory show that 0.78 V at about 200 mA/cm², using H₂ (3 atm) and air (5 atm) can be obtained at 80 °C in PEMFCs containing a Nafion membrane and electrodes with a platinum loading of 0.4 mg/cm². The voltage losses in SOFCs are governed by ohmic losses in the cell components. The contribution to Ohmic polarization (current × resistance) in a tubular cell is 45% from the cathode, 18% from the anode, 12% from the electrolyte, and 25% from the interconnect when these components have thicknesses of 2.2, 0.1, 0.04 and 0.085 mm, respectively, and specific resistivities (Ohm-cm) at 1000 °C of 0.013, 0.000003, 10, and 1, respectively [27].

The operating temperature of the electrochemical devices is very important for both the electrochemical and thermal performance. Although the Nernst equation shows that the open circuit voltage decreases with increasing temperature, the performance at typical

operating current densities increases with increasing temperature due to reduced mass transfer polarizations and Ohmic losses. Some fuel cells are designed, therefore, to work at higher temperatures in order to enhance ion mobility. However, high temperatures can cause chemical deterioration of some devices by enhancing secondary reactions in the electrodes and electrolytes, which may result in a permanent capacity loss. The operating temperature also affects the thermal performance and safety of the electrochemical devices through the sensible heat (heat generated due to the mass of the cell), resistive heating, and heat transfer to the ambient.

3.1. Batteries

In their simplest form, batteries consist of two dissimilar electrode materials (positive electrode or cathode and negative electrode or anode) that are separated by an ionic conductor, which may be liquid, polymer, or solid phase. The characteristic performance of a battery is dictated by the type of electrode material and electrolyte (ionic phase that is usually held in a porous matrix that is often referred to as the separator). Because the electrolyte must be compatible chemically and electrochemically with the electrode materials, the combination of electrolytes and electrodes are limited. For example, commercial lithium–manganese dioxide batteries must use non-aqueous electrolytes because Li reacts rapidly with water.

As mentioned earlier, researchers in small combustion systems often claim a hundred-fold higher gravimetric energy density in liquid hydrocarbons (thermochemical energy available as heat) as compared to the gravimetric energy density of batteries (electrochemical energy available as electricity). In the ideal electrochemical scenario of a pure lithium metal battery, however, lithium is oxidized (discharge) at the anode to form lithium ions (Li^+), releasing one electron. The electron moves through the external circuit to the cathode, where it reacts with the cathode

material, which is reduced. Assuming that each electron per Li atom (which means 3.86 Ah/g) traverses an open circuit voltage of 3.5 V, the gravimetric energy density of Li as a fuel would be 13.5 kWh/kg [46]. This value is nearly identical to that of liquid hydrocarbons. Unfortunately, charge/discharge cycling causes changes in the lithium electrode that reduce the thermal stability of the matrix, causing potential thermal runaway conditions. When this occurs, the cell temperature quickly approaches the melting point of lithium, resulting in a violent reaction. Because of the inherent instability of lithium metal, especially during charging, research has shifted to non-metallic lithium batteries using lithium ions. The energy density diminishes, therefore, because safety dictates that the pure Li must be alloyed with additional elements. Further discussion of lithium-based batteries appears in Section 3.1.1.

The most common properties or characteristics used for the selection of a battery system are gravimetric energy density, capacity, operating voltage, operating temperature, service life, cycle life (for secondary batteries), shelf life, self discharge rate, safety and reliability, and cost. As a first approximation, the practical gravimetric energy density obtained in a battery is 20–25% of the theoretical gravimetric energy density calculated for the battery reaction. The theoretical voltages and capacities of some electrochemical systems used in personal power systems are given in Table 2. The most advantageous combinations of anode and cathode materials are those that will be lightest while giving a high cell voltage and capacity. Fig. 11 is an approximate Ragone plot of several battery chemistries [50].

Batteries are generally first classified as primary or secondary. A primary battery cannot be recharged electrically after discharge; a secondary battery can be recharged electrically, after discharge, by passing current through it in the opposite direction to that of the discharge current. This kind of battery is generally characterized by relatively high gravimetric power

Table 2
Voltage, capacity and gravimetric energy density of some battery systems [45]

Battery type	Anode	Cathode	TGED ² [Wh/kg]	PGED ³ [Wh/kg]	Fraction [%]
Lead-acid	Pb	PbO ₂	252	30–50	12–20
Ni–Cd	Cd	Ni oxide	244	45–80	18–33
NiMH	MH ¹	Ni oxide	240	60–120	25–50
Li-ion	Li _x C ₆	Li _(1-x) CoO ₂	410	110–160	27–40
Li-polymer	Li _x C ₆	Li _(1-x) CoO ₂	410	100–130	24–32

1: MH, metal hydride, data based on 1.7% weight of hydrogen storage; 2: TGED, theoretical gravimetric energy density; 3: PGED, practical gravimetric energy density.

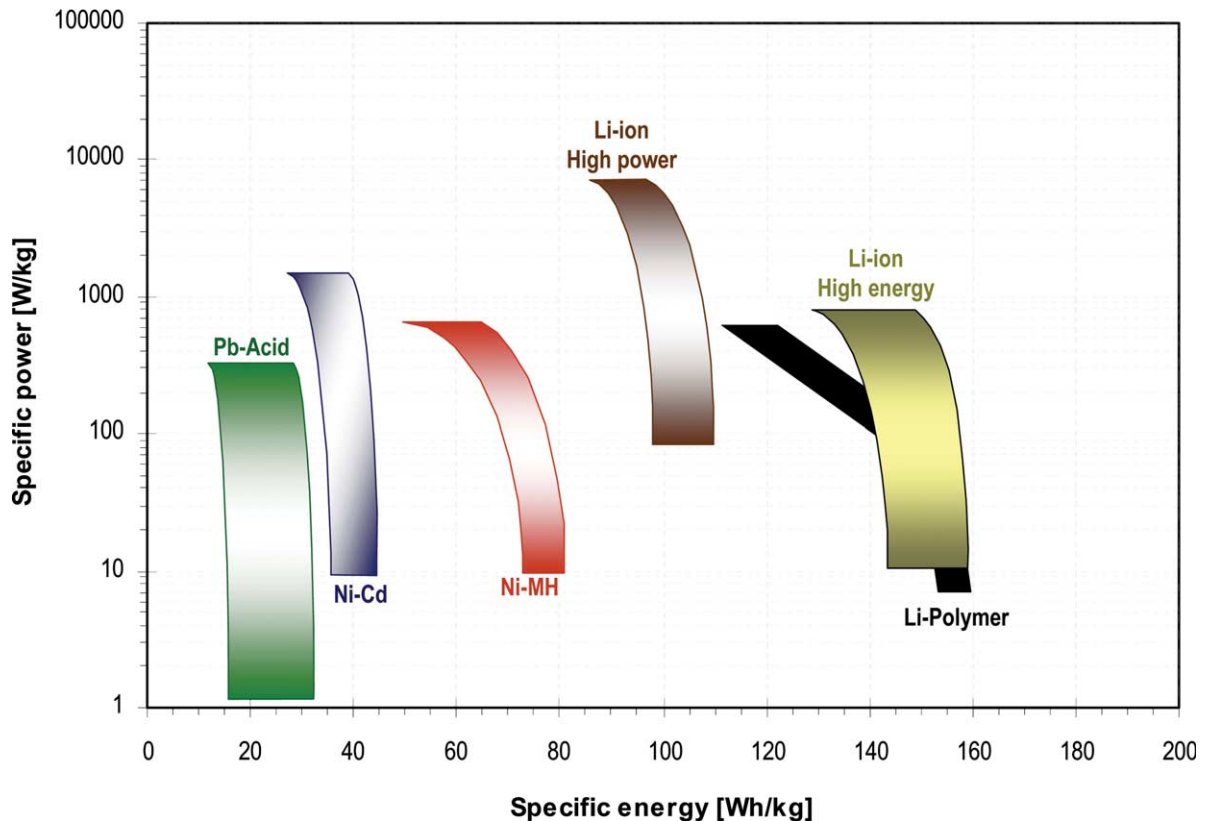


Fig. 11. Ragone plot of some battery systems [50]. Used with permission of MRS Bulletin.

density, high discharge rate, flat discharge curves, and good low temperature performance. However, their energy densities are usually lower, and their charge retention is poorer than for primary batteries.

3.1.1. Lithium batteries

Different battery chemistries each offer distinct advantages but none of them seem capable of providing a fully satisfactory personal power solution. The most advanced rechargeable Li battery that is available is the so-called Li-ion battery. Primary lithium batteries have been used for implantable power for more than 30 years [51], and secondary or rechargeable lithium based batteries are promising power systems for a wide range of applications. These batteries are likely to power most personal electronic devices, as advanced rechargeable Li-based batteries have doubled their energy density over the last 10 years and they continue to improve. Unfortunately, even with continued steady progress, the ultimate performance of batteries cannot reach deep into the future personal power demand window. In addition, the current practice of using cobalt complexes to stabilize the cathode matrix makes the

batteries expensive. Less expensive nickel based cathode materials have received some attention, but are not yet proven [52].

As exemplified in Fig. 12, the true limitation of Li-based batteries for personal power arise because

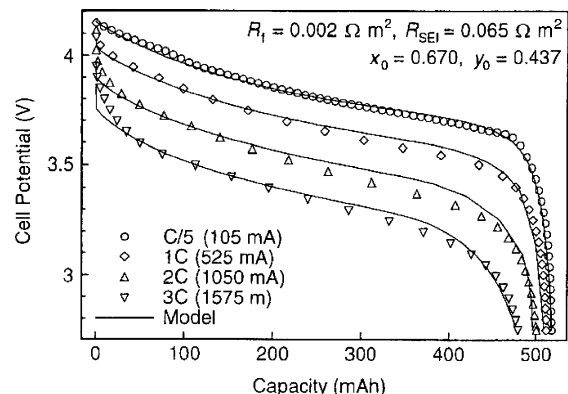
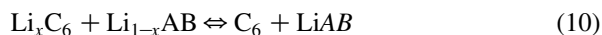


Fig. 12. Sony lithium-ion polymer cell under different discharge conditions (R_f is the film resistance on the collector; R_{SEI} is the solid-electrolyte-interface resistance; x_0 is the initial lithium content in the negative electrode; y_0 is the initial lithium content in the positive electrode; C is the discharge rate.) [53].

the extracted capacity decreases at high power draw [53]. Both experimental results and simple models of this phenomenon show that the decrease is due to the low Li transport rate in the solid-state anode. The cathode-anode barrier (generally a polymer film) reduces ion transport further and increases internal resistance that leads to battery heating (and mechanical changes). In addition, the lithium must penetrate deeper and deeper into the cathode material as the battery discharges, producing a further transport limit. For high power, the highest ion mobility is needed, suggesting liquid or gel electrolyte. However, safety and manufacturing concerns encourage solid electrolyte designs [54]. Lithium metal is attractive as a battery anode material because of its light weight, high voltage, high electrochemical equivalence and good conductivity. Lithium ion batteries use both a lithiated carbon intercalation material for the negative electrode instead of metallic lithium and a lithiated transition metal intercalation compound for the positive active material. The intercalation materials may be generally classified as layered (universal), as channel or tunnel (specific) hosts or as versatile amorphous hosts. Lithium is intercalated reversibly into many host materials without causing major alterations of the structure of the host. The electrolyte is usually a mixture of lithiated salts (e.g. LiPF_6 , LiASF_6 , LiClO_4) dissolved into an organic solvent (e.g. ethylene carbonate, propylene carbonate, ethyl methyl carbonate, dimethyl carbonate). Polyethylene and polypropylene are used as separators. The cathode, anode and overall reactions are, respectively [46]:



Lithium ions move back and forth between the positive and negative electrodes during charge and discharge. The electrochemical process is the uptake of lithium ions at the negative electrode during charge and their release during discharge, rather than lithium plating and stripping. In this case, the gravimetric energy density can theoretically reach approximately 800 Wh/kg [55]. As metallic lithium is not present, lithium ion cells are less chemically reactive and safer, and they have a longer cycle life than cells containing metallic lithium.

The most widespread positive material for Li-ion, lithium cobaltite LiCoO_2 , produces a very high potential (up to about 4.3 V versus Li/Li^+) when

oxidized during charge, but because of the toxicity and high price of cobalt, alternatives are needed. Also, replacing cobalt in the positive electrode with a lighter material would improve the gravimetric energy density, and nickel has been suggested as a promising substitute. LiNiO_2 , a similar oxide using nickel, has a higher specific capacity, up to 200 Ah/kg during the first charge. So far, however, decomposition of the electrolyte as it reacts exothermically with the collapsing delithiated LiNiO_2 matrix has made this alternative unsafe. Delithiated LiCoO_2 is more stable, but delithiation is still limited to 50% for safety in commercial designs [55]. This safety requirement further reduces the effective gravimetric energy density of lithium batteries. Mn based formulations, principally LiMn_2O_4 [56], are promising in terms of electrolyte stability, high working voltage, and low cost. The LiMn_2O_4 spinel system has higher voltage than the others but has lower capacity, at about 148 Ah/kg. The main advantages are the expected lower cost and a better stability on overcharge, but because they are heavy relative to their Li content, the specific discharge capacity is unsatisfactory, particularly for personal power applications [55,57].

As mentioned earlier, LiC_6 is the preferred anode material of lithium batteries. Although some efforts have been made to change the anode material, the standard set by simple graphite is quite high, illustrating the difficulty of improvements in this area. Besides the material properties, the electrodes and cell design are also important areas of potential improvement. In an average design, the cell stack occupies about 70–80% of the total volume (for medium-sized cells) and represents about 80–85% of the total weight [58].

3.1.2. Advances in component technologies

For lithium batteries, it is expected that ongoing research will produce materials with improved gravimetric energy density and lower cost. A particularly promising field is the so-called ‘5 V class materials’, increasing significantly the cell working voltage with little sacrifice in capacity. One of the most cited materials is $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{1.5})\text{O}_4$, which produces an average working voltage of about 4.7 V and maintains more than 120 Ah/kg, when operated with a lithiated graphite negative electrode. However, there is no electrolyte solution currently identified that is able to sustain the high oxidizing potential of this cell. In terms of gravimetric energy density in low-power cells, more than 200 Wh/kg should be attained in a few years, but high gravimetric power density will remain a challenge [58].

Table 3
Some characteristics of rechargeable lithium cells [57]

Li battery couple	Theor. spec. energy [Wh/kg]	Pract. spec. energy [Wh/kg total cell]	Theor. spec. capacity [mAh/kg active mat.]	Pract. spec. capacity [mAh/kg total cell]
Li/Li _x Mn ₂ O ₄	428	120	285 (<i>x</i> =2)	100–120
LiC ₆ /Li _x CoO ₂	570	180	273 (<i>x</i> =1)	136
Li/Li _x V ₆ O ₁₃	890	150	412 (<i>x</i> =8)	309
Li/Li _x TiS ₂	480	125	225 (<i>x</i> =1)	58
Li/S	2600	180 ^a	1672	>200 ^b

^a Based on positive electrode only, with 50% sulfur. Capacity data is for cycle regimen yielding the longest cycle.

^b Results of a prototype of sion power corporation.

Li-ion microbatteries are already well advanced in the lab, and printed batteries using vapor-deposited materials are becoming interesting for small or flexible cells. In the long-term, nanoscale Li-ion batteries could be integrated with devices using templated materials or cells utilizing colloidal-scale self-organization of components, but these will not be designed to produce significant power levels.

The limitation of the extent of lithium intercalation into transition metal oxides is one factor that has stimulated research in lithium–sulfur rechargeable batteries. Table 3 shows some characteristics of rechargeable lithium cells and Fig. 13 shows a comparison by linear scale Ragone plots of Li-ion, Li–S and Ni–Cd batteries [59].

Lithium–sulfur batteries consist of a composite positive electrode (cathode), a polymer or a liquid electrolyte, and a lithium negative electrode (anode). The composite cathode is made from elemental sulfur, carbon black, and a binder. A battery based on the lithium–elemental–sulfur redox couple has a theoretical specific capacity of 1675 Ah/kg based on the active material and a high theoretical gravimetric energy density (2600 Wh/kg), based on the assumption of the complete reaction of lithium with sulfur to Li₂S [60].

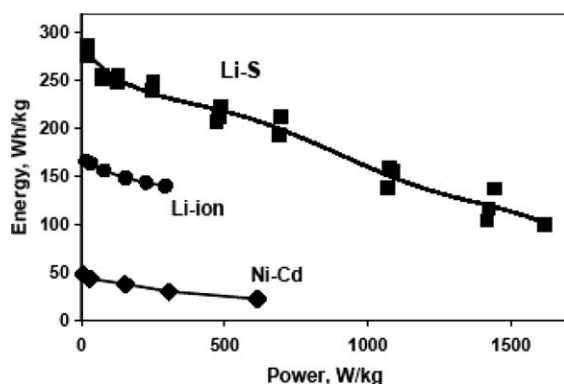


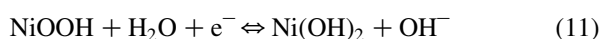
Fig. 13. Comparison by Ragone plots of Li-ion, Li–S and Ni–Cd batteries [59]. Used with permission.

However, Li/S batteries suffer from low percentage utilization of the bulk material and poor reversibility or cycle life [61]. The disadvantages can be attributed to the electrically insulating nature of sulfur and the Li-insertion product and to the loss of active material in the form of soluble reaction intermediates of polysulfides. Even by adding multiwalled carbon nanotubes, which confine polysulfides inside to prevent them from further solution, the improved cycle performance of a sulfur electrode shows only 300 Ah/kg discharge capacity after 50 cycles [62].

3.1.3. Nickel-metal hydride (NiMH) batteries

Nickel-metal hydride (NiMH) batteries cannot match the energy density of lithium-based batteries (see Ragone plot, Fig. 11), but they have some attractive power density features that may be important for some personal power applications. NiMH battery technology advanced substantially with the support of the US Department of Energy's advanced battery consortium [63,64] in support of electric vehicles. NiMH batteries store hydrogen in metal hydride alloys. A nickel hydroxide positive electrode is coupled with a metal hydride negative electrode. During discharge, an electron leaves the negative electrode as the alkaline electrolyte reduces the metal hydride to metal. At the cathode (positive electrode), a hydrogen atom is pulled from the electrolyte into the hydroxide matrix. Both reactions are fully reversible. This charge storage reaction makes the NiMH unit a simple hydrogen transfer battery, in which hydrogen shuttles back and forth between the nickel hydroxide and the metal hydride without soluble intermediates or complex phase changes. For example, during discharge the electrode reactions are [57]:

Cathode :



Anode :



It is the simplicity of the NiMH battery that makes for its high power capability and its long intrinsic cycle life. The recombination reactions of the NiMH battery eliminate the need to monitor and balance the cells individually, which simplifies battery management and reduces its cost. These features and revolutionary manufacturing advances help make rechargeable NiMH commercially viable for powering hybrid vehicles and personal electronics devices where the relatively low energy density is not critical [61]. For the highly demanding personal power applications, however, it is likely that the higher intrinsic electrochemical potential available from lithium technology will be required.

3.1.4. Summary

Based on the maturity of battery understanding, it appears unlikely that fundamental breakthroughs will occur that can produce order-of-magnitude improvements in single cell power performance. In multi-cell battery designs, however, advances in reliability, safety, integration into hybrid systems, optimization of power delivery, and recharge rate, can be significant.

The goal for batteries continues to be higher power with no increase in size, weight or cost. NiMH batteries are currently the standard battery used in hybrid electric vehicles; they offer a gravimetric energy density of about 50 Wh/kg and gravimetric power density up to 1100 W/kg. The NiMH technology is relatively mature, though modest near- to medium-term increases in discharge rate capability are likely, mainly through improvements in engineering design rather than from new materials or nanostructures [62].

Li-ion batteries have specific energies of around 160 W/kg and are expected to show more substantial near- and mid-term increases in capacity, rate capability, and stability. Discontinuous improvements in performance are expected to result from the introduction of new materials, including positive electrode materials. Service life is also expected to improve substantially as one proceeds to smaller and smaller particle sizes making up the active materials within the interface regions.

3.2. Fuel cells

In addition to battery-based electrochemical power, an intense research and development resurgent effort is currently underway in fuel cells. Like a battery, a fuel cell generates electricity directly through electrochemical reactions. Fuel is transformed at the anode, and

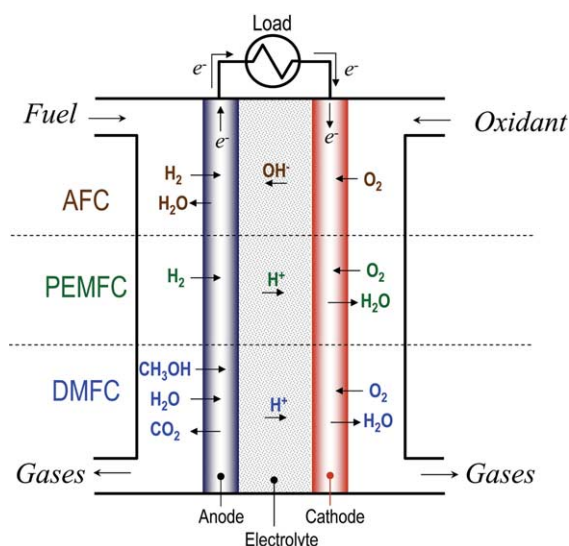


Fig. 14. Basic concepts of an AFC, PEM and DM fuel cell [47].

oxygen is transformed at the cathode. The transformations release electrons that are available to drive a load and ions that are preferentially transported through an electrolyte (see Fig. 14).

The fuel cell type, the electrochemistry, and the temperature of the cell all depend on the electrolyte material. The fact that these devices are electrochemical cells in which the chemical fuel is physically replenished eliminates one of the negative features of secondary batteries, namely the relatively long recharge time. Current development activities in fuel cells stretch from microscale devices meant to power pacemakers and in-body sensors to large-scale systems designed for distributed power in neighborhoods. In-between, there are fuel cell explorations for cell phones, laptop computers, automobiles, and for the auxiliary power on aircraft.

Fuel cell structures and strategies range from low temperature proton exchange membrane systems to high temperature solid oxide devices that can be used in cogeneration environments, and excellent descriptions of these systems are available [27,49]. As already mentioned, there are also efforts to utilize biological processes in fuel cells. Table 4 shows a summary of some differences of the main fuel cell types.

The World Wide Web is littered with references to fuel cells, tutorials on fuel cells, and business evaluations of startup fuel cell companies. Virtually every National Laboratory, Government Agency, and Research University has some fuel cell activity in its portfolio. With this wealth of activity, it is safe to say that no single section can summarize the state-of-the-art

Table 4
Summary of some differences of the main fuel cell types [22]

Type(	Low temperature		Medium	High temperature	
	PEMFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Ion exchange membranes	Mobilized or immobilized potassium hydroxide	Immobilized liquid phosphoric acid	Immobilized liquid molten carbonate	Ceramic
Operating temperature	80 °C	65–220 °C	180–205 °C	600–650 °C	800–1000 °C
Charge carrier	H ⁺	OH [−]	H ⁺	CO ₃ ^{2−}	O ^{2−}
Prime cell components	Carbon-based	Carbon-based	Graphite-based	Stainless- based	Ceramic
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites

PEMFC, proton exchange membrane fuel cell; AFC, Alkaline fuel cell; PAFC, phosphoric acid fuel cell; MCFC, molten carbonate fuel cell; SOFC, solid oxide fuel cell.

in fuel cells. Nevertheless, it is possible to identify the two principal sources of the current enthusiasm for them: (1) they allow relatively low temperature operation with higher theoretical maximum thermodynamic efficiency than heat engines and (2) they are quiet, nominally require no moving parts, and produce electricity directly, just like batteries. The first point means that these devices should be able to use less fuel and produce less carbon dioxide and NO_x emission per kW than do current engines, and the second means that they can be used near people (e.g. in neighborhoods and in backpacks) without disrupting them. Fuel cell demonstrations have confirmed that these advantages can be achieved in practice [e.g. 42,65,66].

The maximum voltage produced by a fuel cell is determined by the thermodynamics of the overall reaction. For a H₂/O₂ fuel cell, for which the standard free-energy change (ΔG^0) is -237 kJ/mol, the maximum voltage is 1.23 V. The electrical energy conversion efficiency of most fuel cells ranges from 40 to 60 percent based on the lower heating value (LHV) of the fuel. State-of-the-art hydrogen-air fuel cells are

achieving 200 W/kg and 115 W/l (not including the fuel storage components) [67]. When attempting to draw significant current through the cell, one encounters limitations very similar to those plaguing batteries, as depicted schematically in Fig. 15 due to the polarizations described earlier.

While there are some significant commercial issues such as cost, reliability, and manufacturability, what fundamentally prevents fuel cells from completely resolving the personal power problem are their relatively low gravimetric energy density and gravimetric power density, as shown in Fig. 5. Again, oversimplifying to some extent, the low gravimetric energy density arises from fuel constraints, and the low gravimetric power density comes from transport limitations across the fuel cell membrane electrode assembly. In a typical fuel cell, the active ions will be protons that come either from hydrogen directly or via some hydrogen-containing compound. Hydrogen, while a very energy dense compound alone, is difficult to store in lightweight fashion. In fact, there is good evidence that among the most effective hydrogen storage modes are ammonia [68] or hydrocarbon fuels [15]. Even when the fuel is hydrogen, extracting the proton from its host at low temperature requires a fairly complex three-phase interface phenomenon involving a catalyst, the fuel, and the electrolyte, all bound in a conductive support structure. The three-phase interface is established among the reactants, electrolyte, and catalyst in the region of the porous electrode. The nature of this interface plays a critical role in the electrochemical performance of a fuel cell, particularly in those fuel cells with liquid electrolytes [27].

When the host is a liquid fuel, additional reforming is generally required, adding to the system complexity and weight and degrading the energy content of the fuel because some fuel must be consumed to provide heat to the reformer. While it is possible to avoid some of these difficulties by operating fuel cells at higher

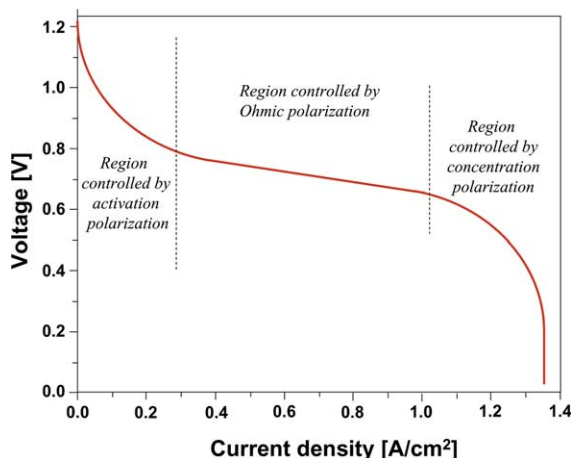


Fig. 15. Typical polarization curve for the H₂/O₂ fuel cell [75].

temperature, such operation reduces the response time of the fuel cell in start-stop operations and adds thermal management challenges. In addition, the materials and high-performance insulation required for current high-temperature fuel cells (MCFC and SOFC) are relatively heavy and bulky, compromising their personal gravimetric power density performance. The basic transport challenge in a fuel cell that limits its gravimetric power density is that the electrochemical reactions occur at a surface electrolyte that must at once allow or encourage ion transport while preventing fuel cross over. In direct methanol fuel cells, for example, this has meant that maximum efficiency can be achieved only at low methanol/water (on the order of 10% or less methanol) concentration in the fuel mixture [69,70]. Hence, the minimum weight of a fuel cell is ultimately governed by the density of its active surfaces and the material required to mechanically support these surfaces.

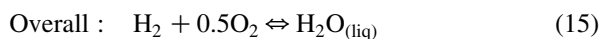
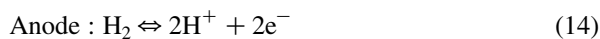
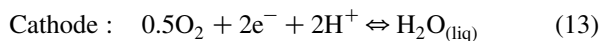
In the current expansion of fuel cell activity it is important to recognize that NASA has been using fuel cells for decades and that the challenges facing fuel cells today are essentially the same as those identified half a century ago [45]. In this sense, as with batteries, the electrochemical aspects of fuel cells are unlikely to yield to fundamental breakthroughs. At the same time, the vast commercial interests involved in fuel cells will be reducing their cost and improving their reliability at the distributed power, automotive, and cell phone scales. Operation of fuel cells on liquid fuels remains a major difficulty, notwithstanding the recent demonstrations in methanol fuel cells [e.g. 71,72] and the claims from several manufacturers that methanol fuel cells are imminent [73,74].

3.2.1. Proton exchange membrane fuel cell (PEMFC)

The proton exchange membrane fuel cells (PEMFC) technology has a high potential for powering personal systems, where it may be able to compete with Li-ion or NiMH batteries. Proton exchange membrane fuel cells are also known as Polymer Electrolyte Fuel Cells (PEFC), and Solid Polymer Fuel Cells (SPFC). In PEMFCs a thin ion-conducting polymer membrane is utilized as the electrolyte. Benefits of solid electrolyte include relatively high gravimetric power density, reduced corrosion and fewer electrolyte management problems compared to liquid electrolytes. PEMFC operate in temperatures where water is in liquid form. Low operating temperature guarantees quick startup from ambient conditions and extremely low nitrogen oxides emission, but then again requires the use of expensive platinum metal catalysts to encourage reaction. Developments in recent years have reduced

substantially the amount of platinum used and the cost of platinum is currently a relatively small part of the total cost of a PEMFC [75].

PEM technology was invented at General Electric in the early 1960s, through the work of Thomas Grubb and Leonard Niedrach. GE announced an initial success in mid-1960 when the company developed a small fuel cell, which applied Nafion[®], a perfluorinated sulfonic acid ionomer membrane invented by DuPont de Nemours Company in 1962, as the electrolyte [76]. PEM fuel cells use hydrogen and oxygen to produce electricity, heat and water. On the platinum surface, hydrogen is oxidized on the anode and oxygen is reduced on the cathode. The proton-exchange membrane conducts protons from the anode to the cathode but not electrons; therefore, electrons are forced through the external circuit, driving the electrical load. On the cathode, oxygen reacts with protons and electrons forming water and producing heat. Half-cell reactions and the total reaction of the PEM fuel cell are presented in Eqs. (13)–(15).



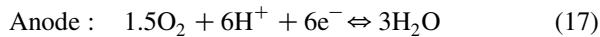
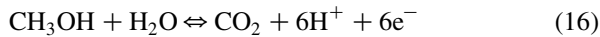
The limitations of the PEM system are high manufacturing costs and complex water management issues. If dry, the internal resistance is high and water must be added to mobilize the system, and too much water causes flooding. Moreover, the PEM fuel cell requires heavy accessories. For large systems mobilize, operating compressors, pumps and other apparatus consume 30 percent of the energy generated [76]. With advances in research, mostly in microfabrication, the problems associated with accessories for PEMFC may be resolved to some extent, but the stack currently has an estimated service life of only 4000 h if operated in a vehicle. The relatively short life span of the stack is caused by intermittent operation. Start and stop conditions induce drying and wetting, which contributes to membrane stress. If run continuously, the stationary stack can have a lifetime of about 40,000 h. The replacement of the stack is a major expense [77].

3.2.2. Direct methanol fuel cell (DMFC)

These cells are similar to the PEMFCs in that they both use a polymer membrane as the electrolyte. However, in the DMFC, the anode catalyst itself draws the hydrogen from the liquid methanol,

eliminating the need for a fuel reformer. A DMFC has an anode at which methanol is electrochemically oxidized to CO_2 and a cathode at which oxygen is reduced to water. The cell reactions are [78]:

Cathode :



Thus, the overall cell reaction is the electro-oxidation of methanol to carbon dioxide and water. The thermodynamic reversible potential (298 K) of the overall reaction is 1.21 V, which is close to 1.23 V for the hydrogen–oxygen fuel cell. Furthermore, DMFCs do not require any fuel-processing equipment and can be operated at ambient temperature and pressure. However, in DMFCs six electrons must be exchanged for complete oxidation, and it is assumed that the oxidation kinetics are slower than in hydrogen oxidation [78].

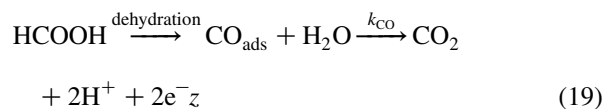
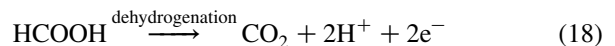
A major problem of DMFCs is fuel crossing over from the anode to the cathode without producing electricity. Methanol crossover, for example, is the process by which methanol diffuses across the fuel cell from anode to cathode. Because the proton exchange membrane that electrically isolates the anode from the cathode is swollen by water, the chemical similarity between methanol and water ensures that methanol can readily permeate the membrane as well. This results in lower conversion efficiency. On the other hand, there are several approaches to reduce methanol crossover. One of them is the regulation of methanol feed concentration above a minimum necessary to provide

methanol to the anode. Fig. 16 shows that the optimal operating concentration is about 2 M or 7% methanol [79]. Above this value, fuel crossover reduces cell efficiency and below it, there is insufficient fuel to produce power at high current density.

Several organizations are actively engaged in the development of DMFCs for powering personal systems capable of replacing high performance rechargeable batteries in the portable devices market. Theoretically, methanol has a superior gravimetric energy density (6000 Wh/kg) in comparison with the best rechargeable battery, lithium polymer and lithium ion polymer (theoretical, 600 Wh/kg) systems [69], but current designs manage only about 10% of this theoretical performance.

3.2.3. Direct formic acid fuel cells (DFAFC)

This fuel cell uses formic acid directly as fuel. Formic acid is a liquid at room temperature and dilute formic acid is on the US Food and Drug Administration list of food additives that are generally recognized as safe [80,81]. Formic acid is a strong electrolyte, and hence, it is expected to facilitate both electronic and proton transport within the anode compartment of the fuel cell. The theoretical open circuit potential for a formic acid–oxygen fuel cell, as calculated from the Gibbs free energy, is 1.45 V. The electro-oxidation of formic acid occurs via a dual reaction pathway, reducing the relative percentage of surface poisoning reaction intermediates [82,83]. Formic acid has two orders of magnitude smaller crossover flux through a Nafion[®] membrane than does methanol [84]. This low crossover flux allows one to use highly concentrated fuel solutions in the DFAFCs and, in consequence, improve the overall fuel cell performance [83,85], even though formic acid (2.086 kWh/l) has a lower gravimetric energy density than does methanol (4.69 kWh/l). According to Marković et al. [86], on a platinum surface formic acid oxidation occurs via a dual pathway mechanism:



The most desirable reaction pathway for direct formic acid fuel cells is via the dehydrogenation reaction (Eq. 18), which does not form CO as a reaction intermediate. In Eq. (18), CO_2 is formed directly, circumventing the CO step, thereby enhancing the

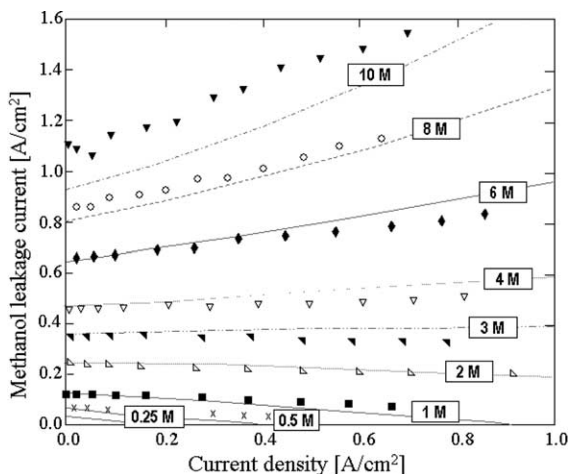


Fig. 16. Methanol leakage current in function of current density [79]. Used with permission.

overall turnover rate. The second reaction pathway (Eq. 19) is similar to that of methanol oxidation, forming adsorbed carbon monoxide (CO) as a reaction intermediate.

Research trends are focusing on the understanding of the system chemistry, the effects of flow rate, high frequency cell resistance, catalyst chemistry, and catalyst activity stability. The fuel cell system needs to be further optimized for formic acid, looking specifically at the transport of formic acid through the carbon cloth diffusion layer and the effect of anodic repulsion versus Nafion[®] content within the anode catalyst layer.

3.2.4. Other fuel cell systems for personal power

Solid oxide fuel cells (SOFCs) are among a class of devices that are being investigated for portable power generation because of their high-energy conversion efficiency, and the possibility of using a wide variety of fuels [87]. The principle of operation of solid-oxide fuel cells is well known [49,75]. The active electrochemical element is a three-layer composite structure consisting of two electrodes separated by a solid-oxide electrolyte. The essential fuel cell reaction is the combination of hydrogen and oxygen to form water. The electrons participating in this reaction flow from the anode to the cathode through an external circuit, generating direct electric current in the process, and the electrical circuit is completed by the flow of oxygen ions from the cathode to the anode through the solid-oxide electrolyte. Such structures can be realized in both planar and tubular geometries [88]. One great advantage of the tubular design of SOFC is that high temperature gas-tight seals are eliminated, as this type of cell works at

900–1000 °C. Alternatives to the tubular SOFC have been developed for several years, notably several types of planar configuration, and a monolithic design. Lower temperature (~600 °C) planar systems are now approaching mainstream commercialization. Due primarily to the high operating temperature, it is difficult to imagine where this technology can be applied to portable applications. Perhaps the next generation of intermediate temperature SOFCs will be more applicable to smaller scale applications but at present the long start up times and elevated operating temperatures limit them to the kilowatt range and above [87–89].

Another fuel cell system that is under study is a biofuel cell. Biofuel cells can use biocatalysts, enzymes or even whole cell organisms in one of two ways [90]:

- (i) the biocatalysts can generate the fuel substrates for the cell by biocatalytic transformations or metabolic processes. In this case the biocatalytic microbial reactor is producing the biofuel and the biological part of the device is not directly integrated with the electrochemical part (Fig. 17(a)).
- (ii) the biocatalysts may participate in the electron transfer chain between the fuel substrates and the electrode surfaces. In this case, the microbiological fermentation process proceeds directly in the anodic compartment of a fuel cell, supplying the anode with the in situ produced fermentation products (Fig. 17(b)).

Recently, novel approaches have been developed for the functionalization of electrode surfaces with

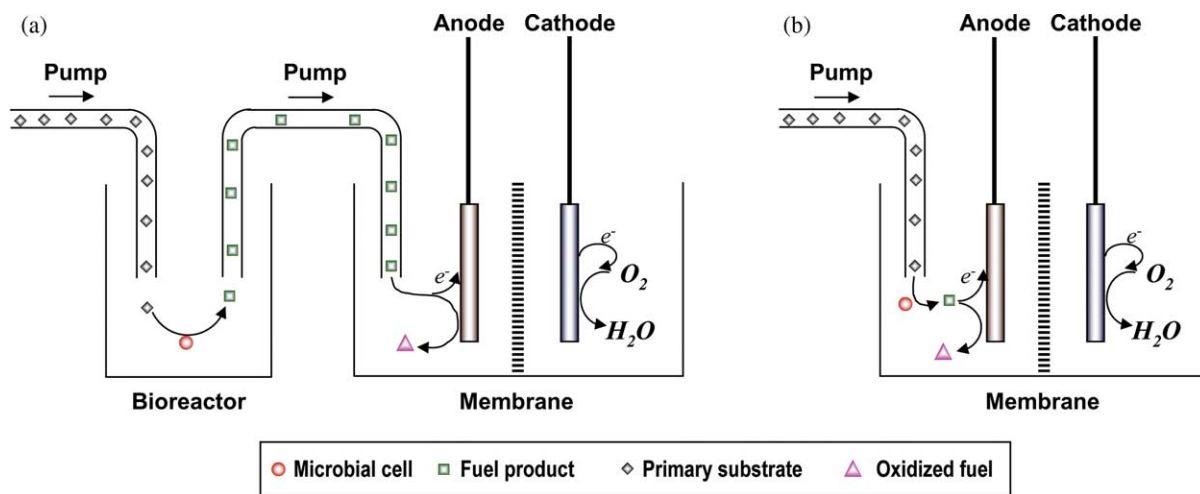


Fig. 17. Schematic configuration of a microbial biofuel cell [90].

monolayers and multilayers consisting of redox enzymes, electrocatalysts and bioelectrocatalysts that stimulate electrochemical transformations at the electrode interfaces. The assembly of electrically contacted bioactive monolayer electrodes could be advantageous for biofuel cell applications, as the biocatalyst and electrode support are integrated. Recent papers summarize advances in the tailoring of conventional microbial-based biofuel cells and describe novel biofuel cell configurations based on biocatalytic interface structures integrated with the cathodes and anodes of biofuel cells [91,92], but none of these designs approach the personal power systems performance target.

3.2.5. Summary

Although fuel cells were first explored as portable power units in the 1960s, widespread interest in portable fuel cells is a relatively recent phenomenon, with significant research efforts by major companies often being less than 5 years old. In such a recently developed market, it is dangerous to expect rapid introduction of fuel cell products. Perhaps the most encouraging sign of a successful fuel cell future is that the driving force behind developments in this sector is the end user. Major electronics manufacturers want greater gravimetric power density and energy for their consumer products, while the military is looking to increase its capabilities using new technology; and both view fuel cells as a possible solution. The true test is still to come, however, as to whether fuel cell technology can compete in all the sectors currently being investigated. More and more prototypes and early series products are being designed and manufactured by an ever-growing number of companies, and at the moment, therefore, the future looks reasonable for some contribution by fuel cells in the personal power realm.

3.3. Conclusions

As technology advances, the power requirements of personal power systems also change. Electrochemical power systems have to meet some requirements such as high gravimetric energy density and gravimetric power density (performance), light weight, and low cost.

The goal for batteries continues to be higher power with no increase in size, weight or cost. Li-ion batteries are expected to show more substantial near- and mid-term increases in capacity, rate capability, and stability. NiMH batteries technology is relatively mature, though modest near- to medium-term increases in discharge

rate capability are likely, mainly through improvements in engineering design rather than new materials or nanostructures.

Fuel cells are assessed relative to the battery technologies they are expected to replace, specifically Li-ion and Li-polymer. Since pricing is a critical factor in whether fuel cells can displace current battery technologies or wall-plug chargers, much depends on finding new materials and on developing low cost manufacturing strategies. These have been the historical challenges to fuel cells since their discovery and demonstration.

4. Thermochemical personal power

Volumetric heat release from liquid hydrocarbon fuels through combustion remains the highest power density mechanism practically achievable for personal power generation, particularly for propulsive needs. In addition, the high temperatures involved in combustion make this process extremely fuel tolerant. For these reasons, heat engines have powered the technological advancements of the mobility revolution, and from the turn of the 20th century forward they have undergone continuous refinement. In general, the target power range of engines is based on centralized power, where an engine supplies power to a few people, a manufacturing plant, or a city. As described earlier, however, when the size of the engine diminishes, so does its performance. For example, a state-of-the-art commercial portable electric generator package is represented by the Honda 1000 EUi, a 1000 W_e peak power system that, based on manufacturer's specifications, can operate for nearly 4 h on 0.6 gallons of fuel. The performance of this generator approaches 20% fuel/electrical conversion efficiency, but its 13 kg dry

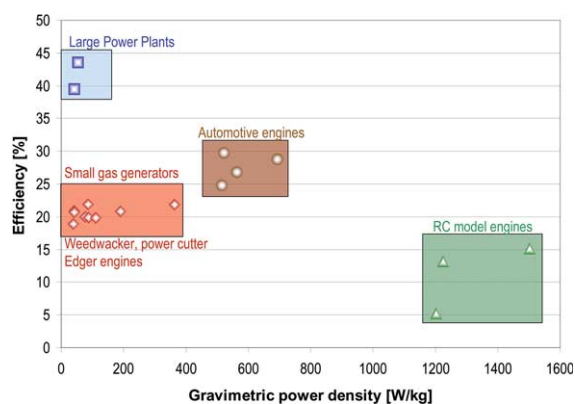


Fig. 18. Currently available commercial engine systems [159].

weight puts it an order of magnitude below the gravimetric power density target shaded in Fig. 5. Fig. 18, a survey of currently available commercial engine systems, confirms a general efficiency decline as engine size decreases to those powering leaf blowers and model airplane engines (this data is based on manufacturers' claimed performance, which can differ substantially from actual performance, particularly for the smallest engines) [93]. This efficiency decline results from increased losses as scale diminishes, without the addition of approaches in design or control to counter this trend.

Substantial recent efforts in microscale combustion [e.g. 13,94] have demonstrated the feasibility of combustion at sub millimeter scales. However, when personal power levels are required, the results of these research efforts raise questions regarding the practicality of systems at such sizes. They suggest, in fact, that engines at the centimeter size have much greater personal power potential than do microscale engines. One simple argument in support of centimeter-scale engines for personal power derives from the relative size of the fuel tank to the engine. For example, 10 h of 100 W operation at 10% efficiency would require approximately 1 l of liquid hydrocarbon fuel. With a 1000 cm³ fuel tank, there is little difference if the engine adds a few cubic centimeters or a few cubic millimeters; the overall system size change is insignificant. Nevertheless, the size-related performance limits of ultra small-scale heat engines have exposed the four principal challenges to high efficiency personal power engines:

- (a) increasing surface-to-volume ratios increase the relative heat losses and increase wall effects that can quench the combustion process or reduce ignition reliability;
- (b) small length scales mean short residence times and little turbulent mixing, making it difficult to fully complete combustion reactions in the time available;
- (c) emissions of noise and pollutants can make these engines irritating to neighbors;
- (d) ancillary equipment for fuel and air delivery, as well as for power conversion, can be much larger than the combustion device itself.

Although these challenges are substantial, the attention to personal power engines has not yet turned to the modeling tools, controls, and advanced diagnostics responsible for the remarkable improvements in engine performance at the vehicle scale. Major engine

manufacturers (both automotive and aircraft) routinely employ three-dimensional numerical simulations and laser-based measurements to improve designs. Optical diagnostics at small-scale are certainly possible and the reduction in spatial and in some cases temporal scales of turbulence should make detailed computations more feasible. Using these methods, therefore, some believe that breakthroughs in our understanding of burning in small volumes, managing the emission from combustion, conversion to electrical power, and, in particular, making small combustion devices compatible with close proximity human use are not only conceivable but achievable in the fairly near term [13].

4.1. Combustion issues

Before discussing some possible strategies for improving the performance of small-scale engines, it is interesting to consider some of the fundamental limits governing the size of a miniature engine capable of producing personal power between 100 and 1000 W. As described by Fernandez-Pello [13], Cadou and Leach [95], and following Waitz et al. [20], the enticing motivation for tiny engines comes from the cube-square law. This concept rests on the assumption that the power per unit air flow is set by the burning rate, which depends on chemical conversion times that are scale-invariant. Hence, the power per unit volume should increase as the scale of the device is reduced because the power-per-unit-airflow scales with the cross-sectional area (length squared) while the mass of the device scales with its volume (length cubed). The cube-square law suggests a continuous power density increase with decreasing size. With even rudimentary heat losses included in the scaling, however, it can be shown that the improvement in power density with decreasing size effectively terminates at characteristic dimensions around a millimeter [95]. Furthermore, as Cadou et al. [96,97] has demonstrated, the promise of the cube-square law is not realized in practice at all, as the performance of small-scale engines does not increase with decreasing scale. In addition to the combustion challenges mentioned above, performance also degrades because of increased friction, reduced turbulent mixing, higher viscous drag, combustion wall quenching, and sealing inefficiencies, among others.

4.1.1. Flame quenching

The early miniature combustion engine studies included substantial discussion of the quenching effect associated with high surface-to-volume ratios. The discussion was driven primarily by the classical

notion of quenching distances for freely propagating flames. The quenching distance is not a fundamental quantity, however, because it depends on the amount of heat lost from the flame to the quenching surfaces. If the heat loss is adjusted, either by heating the surfaces or by heat recirculation strategies [98–100], combustion reactions can be sustained having characteristic length scales well below the classical quench distance [101,102]. Observations of combustion with passive materials at scales below the quenching distance have been observed in several configurations including slot burners [103], excess enthalpy configurations [104], and adiabatically stacked configurations [105,106]. In addition, with catalytic enhancement, surfaces can encourage reactions rather than quench them [94,107,108]. The increased surface to volume favors catalytic approaches and several have demonstrated combustion at scales well below the quenching distance [94,109] or flammability limits [100]. These studies show that there is no fundamental limit to engine size for the reason of flame quenching alone. Surface effects remain critically important, however, as they relate to heat transfer and surface reaction issues.

4.1.2. Turbulence

Cadou and Leach [95] presented a simple laminar flame propagation model, including heat losses, to show that maximum power density would occur theoretically in a chamber of dimensions that approximate the flame thickness. The volumetric power density (VPD) can be defined as:

$$\text{VPD} = \frac{m\nu(\text{LHV})}{V} \quad (20)$$

Where ν is the mass ratio of fuel to mixture, m is the average mass flow rate, LHV is the lower heating value of the fuel, and V is the chamber volume. Using the standard definition of the burning rate:

$$m = \rho_u S_f A_f \quad (21)$$

with ρ_u the unburned gas density, S_f the burning velocity, and A_f the flame area, and assuming that the volume can be estimated by the flame area times a characteristic length L of the chamber, the volumetric power density is:

$$\text{VPD} = \frac{\rho_u S_f \nu(\text{LHV})}{L} \quad (22)$$

This is essentially the equation presented by Cadou and Leach [95] except that the burning velocity is not restricted to its laminar value. In mesoscale combustion

systems, the flow can vary from laminar conditions, through transitional conditions, to turbulent conditions. For example, a previous investigation for a 5 cm³ piston engine characterized the combustion as flamelets in eddies [110], much as would occur for full sized engines. The power generated by engines at this scale can then be considered to be given by the engine displacement times the engine speed:

$$P = A_0 L^3 N_e \quad (23)$$

where A_0 is a unit conversion constant, L is a characteristic dimension of the chamber and N_e is the engine speed. In mesoscale engines, the residence and chemical times are similar, giving:

$$N_e = A_1 \left(\frac{S_f}{L} \right) \quad (24)$$

where S_f is again the flame burning velocity. Traditional turbulent burning velocity (S_f) expressions which assume a thin flame relative to the chamber volume, as described by Clavin and Williams [111], are best suited for the larger mesoscale engines (on the order of 5 cm³ displacement) where appreciable flame wrinkling occurs. In these regions, the turbulence intensity, (v'_{RMS}/S_l) is small and the relation between laminar and turbulent burning velocity becomes:

$$S_f = S_l \left(1 + \frac{v'^2_{\text{RMS}}}{S_l^2} \right) \quad (25)$$

where v'_{RMS} is the root mean square fluctuating velocity and S_l is the laminar burning velocity. The simpler relationship described by Klimov [112] may be valid for the largest of engines at this scale, however the relation requires (v'_{RMS}/S_l) $\gg 1$. This condition is difficult to meet as the scale, and in turn, v'_{RMS} is reduced.

Alternatively, models which consider the flame thickness, such as Daou et al. [113], are perhaps better suited for the smaller scale engines (less than 2 cm³) where the effects of flame thickness cannot be neglected. For thick flames:

$$S_f = S_l \left[1 + \frac{\tilde{L}^2}{2} \int_0^1 \left(\int_0^\eta v(\eta_i) d\eta_i \right)^2 d\eta \right] \\ \approx S_l \left(1 + \frac{\tilde{L}^2}{2} \frac{v'^2_{\text{RMS}}}{S_l^2} \right), \quad (26)$$

where the integral term is related to the flow structure and $\tilde{L}$ is the length scale normalized by the flame

thickness. In this model, the effect on the flame structure occurs primarily through enhanced diffusion. Similar to the description in Daou and Matalon [114], the burning rate is quadratic in turbulence intensity for weak flow intensities, a relation which holds when heat transfer is considered. Based on these limiting cases, the power produced by mesoscale engines can be assumed to fall in the following range:

$$A_2 L^2 S_1 \left(1 + \frac{\tilde{L}^2}{2} \frac{v_{\text{RMS}}^2}{S_1^2} \right) < P < A_3 L^2 S_1 \left(1 + \frac{v_{\text{RMS}}^2}{S_1^2} \right) \quad (27)$$

A_2 and A_3 are unit conversion constants of the same order. In laminar conditions, where $v_{\text{RMS}}^2 \rightarrow 0$, both expressions reduce to that expressed by Cadou and Leach [95]:

$$P = (\text{VPD})L^3 = \rho_u S_f v (\text{LHV})L^2 = A_4 L^2 S_1 \quad (28)$$

where $A_4 = \rho_u v (\text{LHV})$. Therefore, without heat losses (which scale as surface area) the power density is inversely proportional to L , and it increases as the scale is reduced. The increase is not straightforward, however, as care must be taken to consider the concomitant reduction in turbulence intensity and its effect on the burning rate.

4.1.3. Friction

As mentioned earlier, friction is considered a major difficulty at small-scales, and the difficulty is not only related to contact area increases associated with changes in surface-to-volume ratio. There is also a friction increase associated with higher speeds. Yagi et al. [115] analyzed more than 300 small engines (from 50 to 1100 cm³; these are generally larger than personal power engines, but the results appear to extrapolate) for the total frictional power loss at wide-open-throttle conditions. They found that the total frictional mean effective pressure ($\text{MEP}_{\text{friction}}$) can be described by the relation:

$$\text{MEP}_{\text{friction}} = A \left[\phi_1 \left(\frac{V_s N_e}{Z} \right)^2 + \phi_2 N_e^2 + \phi_3 \nu + \phi_4 \right] \quad (29)$$

Where A is a non-dimensional parameter defined as the square root of the product of stroke length and effective crank diameter divided by the bore; Z is the effective valve opening area; V_s is the cylinder volume; N_e is the engine speed; ν is the kinematic viscosity of the lubricants; and the ϕ_i are fitting parameters. Mean effective pressure is the average (mean) pressure which,

if imposed on the pistons evenly during each power stroke, would produce the measured (brake) power output. The frictional MEP is a measure of the average pressure required over the stroke to overcome frictional effects, neglecting the work required to compress the gas. Insofar as the bore, stroke, and crank dimensions scale roughly equivalently as the engine size decreases, A will remain approximately constant. The second term in the brackets shows explicitly that the engine friction work increases with the square of the engine speed. Importantly, smaller displacement engines typically operate at relatively high engine speeds to generate high specific power outputs. Since frictional drag scales as piston velocity squared, friction work begins to dominate systems at small sizes. This effect is muted somewhat by an examination of piston speed. While the crankshaft rotation rate may be in excess of 10,000 rpm, the short stroke lengths in small engines tend to place the piston velocities in a similar range as larger scale engines. In addition, as engine size (and in turn power output) decreases, the constant friction associated with the lubricant viscosity (the third term in Eq. (23)) begins to represent a larger fraction of the available power, leaving less to accomplish useful work. In fact, Suzuki and Ishibashi [116] reported that for a small motorcycle engine they improved performance by increasing the displacement and reducing the engine rotational speed. For the case of small personal power scale engines, it is also necessary to consider the impact of displacement and operating speeds on the combustion process. For efficient mixing and combustion, the flow within the engines should be maintained in a turbulent regime. Therefore, for a given application-driven size constraint, the engine speed must be increased to maintain turbulent flow. That is, for a given power output ($\sim N_e V$), the point at which friction reduction by reduced engine speed has diminishing returns is determined by the effective transitional Reynolds number, $(C N_e V^{2/3})/\nu$, where C is a parameter of order one related to the engine configuration and porting geometry. This condition occurs around 12,000 rpm for a 5 cm³ engine, which is a typical operating speed for miniature engines.

In addition to the aforementioned increase in friction with engine speed and lubrication issues, the role of relative tolerance (Δ/l) is significant. As the scale, l , is reduced, the individual part precision (Δl) must also be decreased commensurately. This can manifest itself in several ways. First, mating part surface roughness begins to have an increased impact. In addition to surface roughness increases, reduced part precision allows crank sliders to have multiple degrees of

motional freedom, resulting in part impact and increased wear. Lastly, runout in bearings and other off the shelf equipment exacerbates frictional problems.

4.1.4. Fuel issues

The above analyses, simplicity aside, only refer to the operative engine element of the power system, not to the fuel, which represents the far larger share of the system volume if long duration operation is planned. As described earlier, for example, assuming a desired 10-h operation at 10–100 W with 10% fuel energy/useful work conversion efficiency, and using a typical liquid hydrocarbon energy density of 12,000 Wh/kg, the system needs between 0.1 and 1 kg of fuel, regardless of the size of the engine. The fuel volume is therefore approximately 0.1–1 l, and an engine of between 1 and 10 cm³ is a relatively small fraction of the overall system volume. In this liquid storage analysis, the added volume of the fuel vessel is not considered because it is small (like a polyethylene water bottle). Should gaseous fuels (some with extremely high gravimetric energy density) be considered for personal power systems, the mass and volume fraction of fuel to fuel storage can be quite low. As an example, hydrogen stored at about 34 MPa (5000 psi) in a 1 l carbon fiber pressure vessel has a mass fraction (considering only the storage vessel and fuel) of less than 10%, as can be seen in Fig. 6. This effect reduces the gravimetric energy density by an order of magnitude even before the conversion device is considered. Consistent with this size scaling, a heat transfer analysis presented by Cadou and Leach [95] shows that the maximum power density possible from a small engine (assuming laminar flow and ignoring frictional effects, etc.) is approximately 1 kW/cm³. If this value were degraded by an order of magnitude to account for the entire engine system (not including the fuel), a 100 W system requires only 1 cm³ of space and a kilowatt unit would require just 10 cm³, still significantly smaller than existing power generation alternatives. With this minimum size, the concept mentioned earlier of enlarging the engine in order to reduce the engine speed while increasing the displacement to achieve the same power with lower frictional loss appears reasonable.

4.2. Fueling comparison between thermochemical power and electrochemical power

When energy conversion (heat engines, fuel cells) rather than energy storage (batteries, capacitors) are considered, several issues related to fuel storage must

be considered: recharge/refill rates and cycles as well as operation mass over time. Thermochemical conversion devices can typically be refilled quickly (e.g. the refill of > 1 GJ takes only a few minutes at a gasoline pump). Recharge cycle limitations in batteries are well discussed in the literature. Thermochemical systems may require some maintenance over the lifetime of the device, but these logistical issues are not easily summarized in a constrained review article focused on power generation technologies. Electrochemical energy storage devices have a constant (or increasing in the case of metal-air batteries) mass throughout the entire operation lifetime. A thermochemical system experiences a reduction in mass during operation until the final mass approaches the conversion device mass itself as the unit is fully ‘discharged’ or emptied of fuel. This difference in mass loss over time between thermochemical and electrochemical systems introduces an interesting comparison. An advanced electrochemical system with a gravimetric energy density of 500 Wh/kg is considered in comparison with a thermochemical system of similar gravimetric energy density. Since, the energy density of a fueled system (fuel + conversion device) is a function of time, however, there exists a crossover point for which the thermochemical system will have a greater gravimetric energy density than will the electrochemical system. For this comparison, a generic thermochemical system with dry conversion mass of 500 g and producing 100 W with an overall efficiency of 10%, is reconsidered. The gravimetric energy density at an infinite operation time will be about 1200 Wh/kg (assuming liquid hydrocarbon fuel). Fig. 19 shows schematically what the gravimetric energy density of the system will be as a function of operation time and shows the

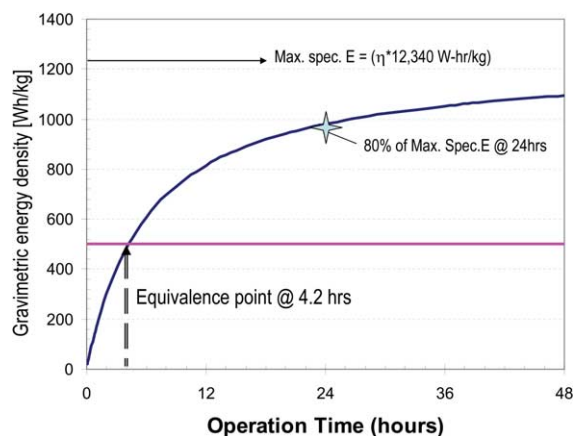


Fig. 19. Instantaneous gravimetric energy density as a function of operation time.

crossover, or energy density equivalence point of 4.2 operation hours for the two systems. The gravimetric energy density of the thermochemical device shows an asymptotic approach to a value that is given by the product of the conversion efficiency and stored chemical energy of the fuel source. In the example shown, the system reaches 80% of this value after 24 h. It should be pointed out that in general this effect of fuel mass loss during operation is not considered in the derivation of gravimetric energy density ascribed to a system. The ‘wet’ gravimetric energy density (which is the minimum value) is reported based upon the initial system weight for a given mission duration length. In many personal power applications, say a liquid fueled power tool or Micro Air Vehicle (MAV), mass loss as a function of operation time can be a significant advantage. In the case of a MAV for long operation times (in contrast to hobbyist applications), for example, mass loss can steadily increase performance of the vehicle, though the redistribution of weight must be considered in the avionics package.

4.2.1. Distributed power

One argument in favor of smaller engines, independent of the fuel volume, is that small engines can be distributed close to the point of application, thereby reducing power transmission losses. This concept is somewhat analogous to the parallelism that biological systems use, where each muscle actin/myosin fiber cycle acts on its own ATP fuel, but the cohesive effort produces the desired macroscale output. As with large distributed-power generation [117] the advantages of distribution might include lower transmission losses (the fuel is transmitted rather than the power) and the opportunity for redundancy. In the case of pumped fuel, the power (P) that can be generated is simply the product of the lower heating value of the fuel (LHV) multiplied by the rate of mass flow (m_f) and the conversion efficiency (η):

$$P = \text{LHV}m_f\eta \quad (30)$$

The disadvantages of distributed power generation are the higher system (including local sense and control) complexity, generally lower efficiency for each element in the distribution chain, difficulties in regulating emissions, and the higher overall mass needed to achieve the same total power as would be achieved from a centralized power supply. Biological muscles illustrate these advantages and disadvantages directly. They exhibit high levels of information complexity (local sense and control) and redundancy, but have

relatively low power/weight performance (judging, for example, by the leg muscle power shown in Fig. 5). As discussed later, specialized adaptations allow insect and hummingbird flight muscles to show substantially higher performance, and similar tuning strategies may be helpful in engine arrays as well. To date, however, very little has been done to investigate or implement this concept at the microscale.

Taken together, the arguments above have been used by several investigators to justify the exploration of the so-called mesoscale engines, which are at least an order of magnitude larger than the MEMS devices described in reference [12]. These mesoscale devices are expected to produce power on the order of 10–1000 W, which is the range referred to in this article as the personal power scale.

4.3. Survey of personal power engines

For the power range and operation lifetimes of interest, it is clear that incremental improvements to existing systems will be insufficient to quickly meet the needs of the personal power community. Higher efficiency and power levels will require hybrid approaches with topping and potentially several bottoming cycles. The role of conversion efficiency is evident in many of the above calculations, showing very clearly the advantage of even small increases in overall conversion efficiency, operation lifetime (Wh/kg), or performance (W/kg) to enhance personal mobility. This can be achieved either through improvements in individual subsystems or through hybrid approaches. As yet, the hybrid approach has not been widely realized because the small engine field still resides in the individual component development phase. In general, combustion devices that operate at the mesoscale can be divided into two groups: static systems and dynamic systems. The following sections discuss briefly power devices from these categories, including those that could be utilized as either topping or bottoming cycles.

4.3.1. Static systems

Static systems consist of some external heat (or light) source and an electricity production mechanism, such as thermoelectrics, thermophotovoltaics, or thermoionics. Recently, the efficiency of these methods has greatly improved making these types of devices much more attractive [118]. In order to reach high power levels, however, static systems often require a complex balance of plant that includes pumps, fans or blowers to bring fresh reactants to the reactor, making

the system dynamic. However, in the interest of organization and to consider the possibility of hybrid cycle analysis, systems are categorized based on the primary energy collection method. As discussed elsewhere in this review, another example that requires system level consideration are high power fuel cells. At the microscale, several fuel cell approaches are being developed that are passive, utilizing diffusion and capillary action for reactant delivery [119]. As these devices move toward higher power levels, purely diffusive transport of reactants becomes rate limiting, and active reactant delivery components are required.

The major limitation to many of the static approaches for electricity generation is either the low power levels that can be expected from passive reactant delivery or a complex active balance-of-plant. It is worth commenting that the well-recognized challenge of seal efficiency for active systems is offset to some extent by the simplicity of the remaining balance of plant, since pumping fuel and air to the reaction zone reduces the need for complex passive designs.

Several thermal-to-electrical power generation approaches exist and many have been significantly enhanced by recent work in micro- and nanotechnology. For example, there are several reviews on the conversion efficiencies of the traditional thermoelectric elements. Recently, the conversion efficiency of an InGaAs monolithic interconnected module (MIM) using reflective spectral control thermophotovoltaic (TPV) has been reported to be 23.6%, with a power density of 0.79 W/cm^2 [118], based on the amount of energy impinging on the cold surface (not in the entire control volume). Another novel energy conversion method, developed at Washington State University, integrates a fluid-vapor cycle with piezoelectric materials and thermal shunting techniques to create the P^3 power generator [120]. The P^3 Micropower Generator [121,122] is an engine driven by low thermodynamic quality (availability) sources. In this engine, a two-phase working fluid fills a cylinder that is sealed at the top and bottom by thin membranes, one of which is a piezoelectric. As heat is transferred to and from the cylinder, the bubble expands and contracts to maintain equilibrium in the fluid. The force from these expansions and contractions of the piezoelectric membrane generates an electrical charge as it flexes. The initial performance evaluation of this device suggests that much development is needed to achieve personal power levels as it generated approximately $0.8 \mu\text{W}$ of mechanical power when driven by 1.4 W of resistive heating power.

Prominent among the small-scale versions of thermal to electrical conversion devices are heat

recirculating strategies [100,108,109] based on the Swiss roll concept [123,124]. The concept of the Swiss roll is particularly attractive for personal power use because the exiting product gases transfer thermal energy to the incoming reactants, increasing the reactant stream enthalpy to greater than simply the chemical energy of the inlet stream. This energy exchange brings the reaction zone temperature above the adiabatic flame temperature for the mixture and reduces the temperature of the exhaust gas stream. A simple convective heat transfer calculation suggests that a temperature difference of approximately 200 K across the inlet/exhaust interface will be needed for practical operation. Sitzki et al. [100], for example, measure an exit temperature on the order of 200°C in their 3.5 turn inconel system. Although these devices are slated for miniaturization, they have been demonstrated at somewhat larger scale, and the early evidence is that combustion using gaseous fuels can be accomplished reasonably well. Most recently, the Swiss roll approach has been coupled with a single chamber fuel cell [125], in which the Swiss roll serves as the thermal packaging. In Vican et al. [109], an alumina ceramic ‘Swiss roll’ microreactor was constructed using a modified stereolithography process. Self-sustained combustion of hydrogen and air mixtures was demonstrated over a wide range of fuel/air mixtures and flow rates for equivalence ratios from 0.2 to 1.0 and chemical energy inputs from 2 to 16 W . Depositing platinum on gamma alumina on the internal walls enabled catalytic ignition at or near room temperature and self-sustained operation down to temperatures of 300°C . Recent studies in miniature heat recirculating burners include the addition of catalytic surfaces [126], computational modeling [108], and some novel concepts for thermally-based flow delivery [127], but so far a practical device at the personal power scale has not been demonstrated. Furthermore, once combustion is stable, there remains the challenge of converting the heat generated to a useable form. Generally, thermoelectric devices are assumed [127] but more recently the single chamber fuel cell is being considered [125]. Independent of the approach, the need for heat recirculation means that relatively large surface area and long residence times are needed. Both of these elements are in opposition to the small sizes desirable for personal power systems.

4.3.2. Dynamic systems

Dynamic power systems contain moving parts and encompass turbomachinery, external combustion

engines, and internal combustion engines. Turbomachines rely on an aerodynamic compression process to increase the combustor operating pressure range for higher efficiency. Usually, they have very high operating speeds which places a large burden on bearing life and performance. External combustion engines are attractive because the combustion process can be optimized without considering the inherent complexities of the engine workings. While these external combustion approaches (including Rankine cycle engines) look promising to deliver high efficiency, they suffer from low gravimetric power density. This deficiency will make these systems difficult to utilize in personal power applications. Internal combustion engines typically have quite high gravimetric power density, which is attractive to meet personal power needs. Unfortunately, frictional, sealing, and combustion losses have made it difficult to reach the efficiency levels required for desired operation times. The fact, however, that radio-controlled model engines of approximately the personal power scale do operate at low cost (leading to poor tolerances and part count limitations) suggests that these issues can be overcome with attention.

4.3.2.1. External combustion approaches. Small-scale external combustion Stirling-type engines could be produced, though heat transfer scaling suggests that such engines are less promising at small sizes [128,129]. One advantage to external combustion engines, as well as turbomachinery, is that the combustor operates continuously. It has proven to be a challenge, however, to run a small-scale (on the order of centimeters) continuous combustor on liquid fuel. While the typical approach is to spray the fuel as tiny droplets, this method is problematic at small sizes where the wall surfaces are so close together that substantial impingement and minimal air entrainment occurs. One alternative being explored is to burn the fuel after it is delivered via electrospray onto a catalytic mesh [130,131]. Another concept is to inject all or a portion of the liquid fuel directly as a film on the solid surfaces where high heat transfer from the combustion products occurs. The evaporating fuel keeps the chamber cool while preventing heat loss [132,133], providing a built-in thermal management capability. Preliminary research with the film combustor has shown the importance of fluid dynamics within the combustor to maintain flame stability [134,135]. Beyond the combustion process, the issues of sealing and parasitic frictional loss also exist for external combustion engines. Despite these challenges, several Stirling

approaches are in development, including a unit at DEKA [136], a 100 W engine in Japan for underwater applications [137], and a 25 W unit by Sunpower, Inc. [138]. Sunpower, Inc. [138] has a development history of free-piston Stirling technologies (coolers and engines). Their small machine is projected to have efficiency greater than 50% of Carnot's efficiency and a projected gravimetric power density of approximately 90 W/kg. This power density is not sufficient for personal power, and the extraction of electrical power is further complicated by generally low operation speeds (on the order of 1000 shaft rpm).

Peterson [10,128] carried out a study to determine the lower size limit at which a practical thermomechanical engine can be developed. For regenerative heat engines, (i.e. those that utilize the enthalpy of hot product streams to preheat reactants or walls), this critical size is about 1 mm. Below this size, the author notes that thermoelectric systems are more practical. The analysis is based on a heat transfer parameter (λ) that relates the amount of heat transferred by moving a working fluid through a tube to the amount transferred by the solid tube itself [139]:

$$\lambda = \frac{\dot{Q}_k}{\dot{Q}_{\text{fluid}}} = \frac{\left(\frac{k_s A_s}{L_s}\right)(T_H - T_L)}{\dot{m} C_p (T_H - T_L)} = \frac{k_s A_s}{\dot{m} C_p L_s} \quad (31)$$

A Stirling cycle engine is selected as the representative thermomechanical cycle for this analysis as a closed form solution can be derived for the efficiency that shows its relationship to the system length scale:

$$\eta = \frac{W_{\text{out}}}{\dot{Q}_{\text{shunt}} + \dot{Q}_{\text{HeatEngine}}} \propto \frac{L^3(1/L)}{L + L^2} \propto L \quad (32)$$

Two loss terms are included in this solution: axial heat loss from the high temperature reservoir (assumed to be linear) and heat transfer within the regenerator. An expression is provided that gives the thermal efficiency of the Stirling engine as a function of the temperature ratio, the regenerator effectiveness (which is secondarily a function of length scale), and the conduction parameter (which is affected primarily by length scale). The theoretical efficiency is found to decrease with scale. For materials with high thermal conductivity, poor thermodynamic efficiency results as engine size is reduced to less than 1 cm, a result that is in accordance with the observations of Cadou and Leach [95] for internal combustion engines.

4.4. Turbomachinery approaches

An alternate method for combustion-based propulsion, or for producing rotary motion for electricity generation, is to use continuous combustion, as in a gas turbine. Small-scale power extraction concepts using both Brayton and Rankine cycles are being developed [21,22,140–144]. Gas turbines appear attractive at small sizes due to the cube–square law previously noted, potentially delivering very high gravimetric power density levels. Unfortunately, increased heat transfer and relatively low fabrication precision have presented significant challenges. The reduction in scale increases heat transfer rates so that thermal energy transfers rapidly from the combustor to the intake and compression regions, reducing the compressor efficiency. The low fabrication precision further reduces the effective pressure ratio and overall efficiency of the device. High speed bearing systems with very little runout and low power requirements represent another difficulty. A recent review describes many of the underlying issues in the development of small-scale turbomachinery [145] while another review surveys the field of microturbomachinery [146]. Of the challenges listed above, these reviews demonstrate that heat transfer from the turbine stage to the compressor is the most significant obstacle toward operation [147].

4.5. Internal combustion engine approaches

A University of California, Berkeley group has for several years been pursuing a miniature rotary (Wankel) engine design based on several favorable features discovered at the mesoscale [148,149]. The rotary engine consists of a triangular rotor (piston); the apexes maintain a sliding contact with an epitrochoidal chamber forming three distinct chambers within the epitrochoidal housing. The engine operates in a four cycle process, where the rotor motion brings in a fresh intake charge, compresses the fuel/air charge and is then pushed forward (acting on an eccentric throw) when the charge burns and finally exhausts the reaction products. This engine is capable of:

- (i) high gravimetric power density: the rotor operation permits three charges per revolution, which results in high power per volume;
- (ii) self-valving operation: the rotor acts as a valve, and controls the timing of the intake and exhaust;
- (iii) simple design: the engine consists of only a front plate, epitrochoid housing, back plate, rotor, internal gear, spur gear, and shaft;

- (iv) planar geometry: simplifies fabrication and favors any of the standard precision fabrication techniques;
- (v) rotary output: the power output is in the form of rotary motion, ideal for powering an electric generator.

A rotary engine already developed [105] was designed for operation around 20W, and 3 W operation on compressed hydrogen and air has been achieved. Although this engine operates below the personal power target, it has faced the same scaling issues that occur in larger engines. In particular, experiences with the mini-engine have demonstrated the importance of diagnostics and modeling in the design process, as well as thermal management, ignition location, and exhaust treatment during operation [106,149]. The miniature rotary engine has more recently been powered by liquid fuels and power levels of about 5 W have been achieved although at very low efficiencies because of incomplete combustion and poor seal effectiveness [150]. Liquid fueled, naturally aspirated operation is critical for achieving personal power goals, and liquid fuel introduces a range of new problems for the rotary engine, including wall wetting, fuel evaporation time, lubrication contamination, and flame stability when faced with latent heat absorption by the liquid. Furthermore, operation with liquid fuels allows for lubricant addition without bulky lubricating systems.

The University of Michigan is developing a portable power generation systems based on the micro internal combustion swing engine (MICSE) [151]. The system has a projected mass of approximately 54 g (non-fuel) and volume of 17 cm³. A swing engine is a rotationally oscillating free-piston engine in which combustion occurs in four chambers separated by a single rotating swing-arm in a single base structure. The resulting efficient use of both chamber space and system mass permits lower weight and smaller size at the same power as compared to linear free-piston engines. Successful development of such integrated microengines and generators requires careful consideration of key flow and combustion issues. Some recurring challenges for this approach include sealing, controlling input spark energy and successfully extracting electrical power from the oscillatory nature of the ‘piston’.

Several 2-stroke approaches are also in development because of the potential for high gravimetric power density levels. Georgia Tech has demonstrated the most significant power output to date in a unit designed to operate with a free piston and to effectively integrate an

electrical generator. An extensive modeling effort was utilized for port design and combustion modeling [152]. The results of the model were used to make improvements in power extraction, however losses due to sealing inefficiency and fuel utilization remain troublesome. These observations were echoed in the development of helix-spring-returned 2-stroke engines at Aerodyne [153]. The key to the spring-return work is the removal of many traditional engine components, which are a large source of friction. The piston is free to translate without a connecting rod or crankshaft and the piston motion is transduced to electrical power through an alternator located below the helical spring. A similar approach was followed by Aichlmayr et al. [154,155] who developed a small homogeneous charge compression ignition (HCCI) engine. HCCI engines are attractive because of low pollution levels and good fuel utilization [156]. Unfortunately, for HCCI operation, the intake charge is quite lean (<0.7), reducing the potential power output. Increased operation speed is the simplest way to increase power output on the macroscale, but this is difficult at the mesoscale because of poor exhaust scavenging and limited residence times for complete combustion.

While research into the above-described novel mesoscale engine designs is creative and exciting, there are already conventional commercial engines at this size. Many 2-stroke engines exist, for example, in the 10–1000 W levels for the delivery of shaft torque for radio controlled aircraft, leaf blowers and power tools. Radio-controlled (RC) model airplane and model car engines produce power in the range from 50 to

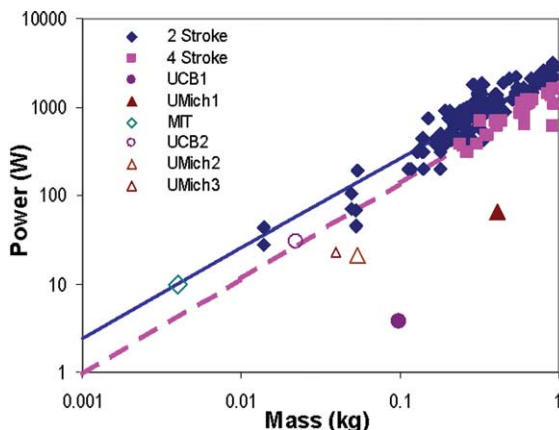


Fig. 20. Power output of 2-stroke and 4-stroke engines weighing less than 1 kg. Solid symbols correspond to existing engines while open symbols correspond to engines in development [96]. Used with permission.

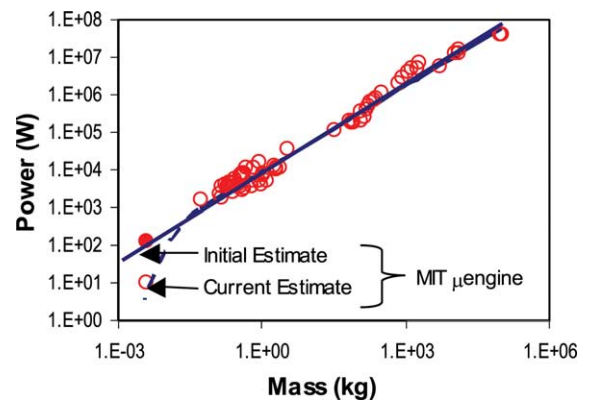


Fig. 21. Power output of larger IC engines (2 and 4 stroke) [96]. Used with permission.

1000 W in very small packages, and small utility motors (e.g. chainsaws) also represent commercially available and reliable personal power devices with high output capability. Cadou et al. [96] surveyed 200 engines with mass below 1 kg and found that the power-to-weight ratio is nearly constant across a wide range of engine sizes, with 2-stroke engines having slightly higher performance than 4-stroke models. Incidentally, this reference also shows that the exploratory gas turbine engines described in the preceding paragraphs are far below the power-to-weight of the commercial engines. Even after enormous effort, the MIT microturbine that was originally projected to achieve 100 W in a few grams is now expected to manage perhaps one-tenth this value (without fuel). It is clear from Figs. 20 and 21 that engine scale has a significant impact on engine efficiency. As mentioned earlier, although the impact of scale has been discussed in some detail [157], without a complete diagnostic evaluation of small

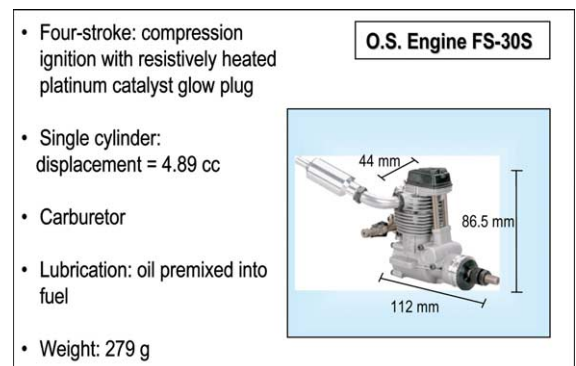


Fig. 22. Photograph of the O.S. Engines FS-30S [93,110,159]

engines, it is difficult to distinguish the impact on overall engine efficiency among the many loss terms, including volumetric efficiency, seal efficiency, combustion efficiency, and parasitic losses due to friction.

As a specific example of an RC model engine, Fig. 22 shows a photograph of the O.S. Engines FS-30S, a representative modern, mass-produced model engine [93,110,158]. The engine is a single cylinder, 5 cm³ displacement 4-stroke design, with single intake and exhaust valves driven by pushrods. The piston has only one piston ring. In the O.S. engine, a carburetor handles fuel delivery. The air–fuel ratio is varied by manually adjusting a needle valve. High temperature exhaust gas pressurizes the fuel storage tank. The pressure driving the fuel through the carburetor is influenced, therefore, by both the hydrostatic pressure of the liquid fuel and by the temperature and pressure of the exhausting products. While this design has the advantage of simplifying the balance of plant, it contaminates the fuel supply and can produce inconsistency in the fuel/air mixture delivered to the engine. Ignition in the engine is initiated by a resistively heated glow plug wire incorporating a platinum catalyst, but once the engine has reached a steady state operating temperature, electrical energy to the glow plug is no longer necessary. The retained heat of the glow plug continues to provide a catalytic hot spot for ignition within the engine cylinder [159]. Since, ignition in these engines is initiated much in the same manner as HCCI engines, they are plagued by the same ignition timing challenges. To control the ignition timing, indirect methods must be used (for example, those which alter the compression process or the fuel oxidation kinetics). To further complicate the issue of ignition, cyclic variability is large, which results in a large fluctuation in the ignition and subsequent combustion process, producing high cycle-to-cycle mean effective pressure variance. These findings, most notably cycle to cycle variation in pressure rise, were recently observed in a similar scale (5 cm³) wankel type rotary engine [160].

Lubrication of the engine parts is handled by premixing the fuel with oil. This simplifies the engine design, however, the low vapor pressure oil condenses rapidly when it cools in the atmosphere, forming a great deal of condensate, leaving significant oily deposits on surfaces in the immediate surroundings of the engine. An additional disadvantage of this lubrication design is that it relies on leakage past the piston ring and flow of oil-laden fluid into the crankcase for lubrication of the connecting rod and crankshaft bearings. This strategy increases significantly the crevice volume, leading to a

reduction in cylinder pressure during compression and combustion, thereby reducing efficiency and performance. Under some conditions, the reduction in contact forces at smaller scales may allow for the natural lubricity of liquid hydrocarbons to be utilized as lubricant. In any case, the elimination of bulky lubrication machinery should be attempted whenever possible. Fuels for model engines are generally composed of methanol (CH₃OH), nitromethane (CH₃NO₂), and oil. Typical mixtures are 10–20% (by volume) oil, 0–50% nitromethane, and a balance of methanol. Ideally, the oil component of the fuel does not contribute to the heating value of the fuel. Synthetic-based oils, castor-based oils, and mixtures of the two are used for lubrication currently. Because of their proprietary nature, it is difficult to find any useful information about synthetic-based oils. Castor oil is a very good natural lubricant, having a coefficient of friction with steel on steel of 0.095 [161]. It is a thick, clear-yellowish oil extracted from the seeds of the castor bean plant, *ricinus communis*. Its composition is approximately 89% riciniolic acid, with approximately 11% other fatty acids [162]. As it is heated, castor oil forms complex polymers, which continue to provide excellent lubrication properties; this results, however, in the formation of high molecular weight compounds that tend to create a coke or varnish. Castor oil has a flash point of 229 °C and the spontaneous ignition temperature is 449 °C, significantly higher than most polyalkane glycols. Most synthetic oils boil and burn in the combustion chamber as their flash point is reached, whereas castor oil continues to lubricate with the above-described formation of heavier compounds. Small engine operators trade off high temperature lubrication versus coke formation. In RC engines, methanol is used to keep engine temperatures low so that the castor oil does not break down and form coke. It is also interesting to note that castor oil is being used in Brazil as the basis for biodiesel fuel because its heat of combustion is 39.5 MJ/kg. Thus, if burned, castor oil would contribute greatly to the heating value of the fuel mixture, but as noted above, the oil is presumed resistant to combustion because of its polymerizing behavior. It is difficult to confirm this presumption, however, which complicates the computation of thermal efficiency. Hence, the role of lubricating oil in RC vehicle engines requires some further study.

The results of miniature commercial engine characterization studies are limited, but they appear to show that these engines operate overall near stoichiometric, a surprising result to anyone experiencing the fuel and oil laden exhaust ejected by these engines. It seems

plausible, therefore, that combustion in these small engines is some combination of a partially-premixed core, initiated by catalytic compression ignition, and wall film combustion. The existence of liquid films in full-size automotive engines is problematic because films can lead to lower fuel economy, higher soot emissions, and increased deposit formation. Further diagnostic intervention is required to confirm if these same effects occur for the mesoscale, but such investigations are beginning to develop [93,96,97,163].

One of the under-appreciated difficulties with optimizing small engines is the lack of standardized test and measurement tools at the appropriate scale and precision. Most previous work in small engine diagnostics uses only thermal probes, imaging, or sample collection and analysis [e.g. 100,105,106]. Non-intrusive optical methods are, however, potentially very useful in small devices where physical probes would perturb the system under study. Some investigations have demonstrated infrared imaging measurements in a small rotary engine [149] and temperature measurements by coherent anti-Stokes Raman spectroscopy (CARS) at the exit of a small film combustor [133], but much more can and should be done. Optical diagnostic development has been utilized to study flame front structure and speed [163] as well as to examine product species at the ends of reaction vessels [164]. Unfortunately, the short optical path length and contamination

by unburned lubricant makes measurements in liquid fueled, mesoscale combustion engines difficult. Film thickness measurement techniques that have been developed for macroscale engines may have applicability in mesoscale engine development [165]. A NMR technique developed by Reimer [166] may also be relevant to engine developers. In addition to optical techniques, several small-scale pressure sensors are now available that can be utilized as a mesoscale engine diagnostic [167].

At a slightly larger scale than the RC engine, are the advanced portable commercial engine products and generators manufactured, for example, by the Honda Corporation [168] and others, for application in such equipment as leaf blowers, chainsaws and weed eaters. In order to illustrate existing designs that incorporate all of the elements needed in a thermochemical personal power system, Fig. 23 shows an orientation-free small utility engine (750 W) and a portable electric generator. According to the manufacturer's specifications, these engine perform at approximately 20% efficiency, but they are at least a factor of 10 larger than the ideal personal thermochemical power system. Including the fuel tank, the orientation-free engine has a power density (mechanical) of approximately 225 W/kg and, assuming the fuel needed for 10 h of peak torque operation, it can deliver 1190 Wh/kg. Note that these estimates indicate that the balance of mass to reduce



Fig. 23. Orientation-free small utility engine and small genset; both use approximately 0.6 l fuel tanks [168].

sound levels and to convert from mechanical to electrical power is significant. In the case of the Honda EU1000i Handheld Portable Power Generator, a 50 cm³ engine is used with a dry weight of 5.45 kg to supply mechanical torque. The resulting mass of the generator is more than double the weight of the engine.

Walker et al. [169] tested a 1000 W genset system alone, and they found that, as expected, its efficiency increased with load, exceeding 14% thermal to electrical efficiency beyond 700 W. These values would put this device approximately a factor of three below the personal power generator challenge described in the introduction, but they show the relatively high performance possible with attention to small-scale combustion system design.

Before summarizing thermochemical power systems, it is worthwhile mentioning commercial devices that have already demonstrated successful implementation of some of the thermochemical power conversion concepts described earlier as being actively in research. For example, the concept of a mesoscale catalytic burner is already implemented in catalytic propane heaters [170]. These heaters use a catalyst mat that both promotes propane/air reaction and acts as a radiant surface. The Coleman company propane heater [170] produces nearly 1000 W in a unit weighing around one kilogram. Another novel use of a miniature catalytic system is the portable butane soldering iron [171]. This device reacts butane across a catalytic grid and the heat is transferred to the soldering tip allowing remote repairs far from an electrical outlet. Both of these systems have no moving parts and they show that the heat release portion of the power system is not necessarily the most challenging. Rather it is the efficient conversion of this heat into propulsive or electrical power that can present the major difficulties.

4.6. Conclusions

An examination of a traditional Ragone diagram indicates that for maximum gravimetric power density levels combined with realistic operating duration (as opposed to burst power from flywheels and super-capacitors), thermochemical engines are hard to surpass. As the scale is reduced, however, there are several mechanisms that if not appropriately addressed with design changes will reduce substantially their overall conversion efficiency. Nevertheless, largely due to the integrated balance of plant incorporated by many heat engines, it does not appear that technologies currently exist to supplant thermochemical engines from a gravimetric power density standpoint. It should

be further pointed out that thermochemical engines are quite flexible in their power delivery method, being capable of producing electrical power (through a generator) or mechanical power either as a rotational torque or mechanical thrust (pressure). Hence, improvements in mesoscale engines can impact significantly the area of personal power, but only through efforts directed towards a better fundamental understanding of the processes that occur within these systems. Perhaps more importantly, hybrid designs that most efficiently utilize the chemical availability of hydrocarbon fuels can be developed. As an example, an internal combustion engine could serve as a topping cycle from which mechanical work is extracted. Some of the high availability exhaust can then be harnessed to generate electrical power as a first bottoming cycle. Subsequently, lower availability energy is utilized to further enhance the electrical work generated or could generate steam (or space heating) as a cogeneration unit. These types of approaches are carried out every day in large-scale power production facilities (nuclear, coal) and where logistical supply is difficult (e.g. submarines and ships). In order to enable personal mobility, these approaches can be taken in highly integrated mesoscale systems to increase gravimetric power density and gravimetric energy density.

5. Biochemical personal power

Although concepts for utilizing biological activity as part of power systems are not unheard of, biological approaches for the personal power range are virtually unexplored. For example, the use of bacteria to create combustible gases from waste streams via digesters is well-known and approaches using bacteria and sunlight to produce hydrogen gas for fuel cells at efficiencies far higher than can be achieved with simple electrolysis have also been demonstrated [172]. Biological enzymes are also being explored as tools for in situ low temperature reforming of liquid fuels in fuel cells without resorting to precious metal catalysts [173,174]. Additionally there are efforts aimed at creating biological fuel cells. In some cases, the inherent electrochemistry of human cells is exploited and energy is harvested directly to produce a continuous electrical power source in a living system [175,176]. In other applications, a micromachined microbial fuel cell is being developed as a potentially implantable energy source for microsystems [177]. *Saccharomyces cerevisiae* is used in this case to catalyze glucose to fuel for the 0.51 cm² cell. Electricity is then produced by the overall redox reaction, yielding an open circuit

potential of 343 mV and 0.5 W/m^3 across a 10-Ohm load. These cell-level microscale devices are limited to tiny power levels, suitable for powering remote sensors or perhaps a pacemaker. There do not appear to be any major research efforts underway intended to utilize the machinery of biological metabolism for generating power at the PPS scale, however, harnessing the useful function of cells, particularly cardiomyocytes and jellyfish cells, as actuators in bio-microfabricated hybrids is being explored [178]. The formic acid fuel cell is considered by some researchers to be a biologically inspired system because formic acid is produced naturally in ants [179]. In addition, there are some explorations of glucose-based fuel cells that will use natural tree sap as their fuel [180]. Although both formic acid and glucose could be used in larger fuel cells, they are not concentrated enough in nature to supply personal power levels.

One challenge of biochemical power strategies is that after the release of energy using biological or biologically inspired means, it is then necessary to convert this energy release into useful work. In the macro world, chemomechanical energy conversion is rare but at the cellular scale it is more common. For example, biological motors such as ATPsynthase and flagellar motors create rotary motion by extracting energy from an ionic current (H^+ , Na^+). A subunit of ATPsynthase can rotate at up to 1000 rpm. Flagellar motors, found on the cell membranes of bacteria such as *E. coli*, are about 45 nm in diameter and can generate speeds of 6000–60,000 rpm at $7.46 \times 10^{-7} \text{ W}$, representing a power density (without fuel) of 3 kW/kg . This kind of biomolecular motor model has been demonstrated [181], and the physics of such systems have been described in several publications [e.g. 9,182,183]. More recent work to examine the efficiency of the F1-F0 motor pair at ATP synthesis and hydrolysis reactions hints at interesting future research directions. In one example, Itoh and coworkers [184] have attached a magnetic bead to the portion of ATP synthase known as F1-ATPase, and have actuated this system by an external magnetic field to synthesize ATP. The process is nearly reversible and an average efficiency of 77% has been demonstrated with a torque of 40pN-mm at a maximum speed of 7800 rpm. Given the volume of the F1-ATPase reaction chambers (several femtoliters), this results in a power density of more than 1 MW/m^3 , better than the best nuclear reactors. Again, however, these biomolecular motor efforts are aimed at tiny power levels that can be scavenged from naturally occurring sources and include a balance of plant which may prove to be more

challenging than that of the electrochemical or thermochemical areas. The organisms will require a thermally stabilized, contaminant free environment, that includes feeding and waste removal. The personal power demand, as outlined earlier, requires large absolute power levels and will require special attention. For example, a ready-made chemomechanical biological power generator exists in the flight muscles of hummingbirds and insects, but it is not at all clear how to exploit this biological performance in a controlled manner. The following sections are intended to introduce some of the parameters by which such exploitation might occur.

5.1. Biochemical energy efficiency

All living cells must have an energy source, and that energy must be in a form that can be used by the cell. In animals, the mitochondrion is the organelle responsible for energy transformation. In the mitochondrion, energy trapped within carbon-based fuels is released and eventually converted to adenosine triphosphate (ATP). The hydrolysis of ATP, into adenosine diphosphate (ADP), releases energy, which drives basic reactions culminating in cell growth, nerve impulses, muscle movement, and other fundamental cellular and organismal functions [185].

According to the Huxley model [186], and substantiated by more recent studies [e.g. 187,188], the consumption of ATP during muscle contraction produces a conformational change in the myosin molecules as they cyclically ratchet along thin actin muscle fibers. The conversion of glucose into ATP is considered a very efficient process, achieving 40% conversion efficiency on an energy basis at standard conditions [185]. The ATP to muscle movement efficiency can be greater than 30% [189], which suggests that a very respectable 12% glucose-to-mechanical output efficiency is possible. Actual practical organisms have been measured to achieve conversion efficiency close to 10% [190], but it is important to contextualize this value and remember that this efficiency is achieved at low (i.e. body) temperature relative to that of a typical heat engine. Without high temperatures, it is very difficult to oxidize complex fuels in either thermochemical or electrochemical systems. Even if it was possible to catalyze conversion reactions at low temperature in a heat engine, the Carnot cycle operating between a hot thermal reservoir at body temperature ($T_h = 310 \text{ K}$) and a cold reservoir at typical air-conditioned temperature ($T_c = 295 \text{ K}$) could not

manage an efficiency ($\eta_{\text{carnot}} = 1 - T_c/T_h$) of even five percent, and using the more realistic efficiency of the endo-reversible engine operating at maximum power [191] ($\eta_{\text{endo}} = 1 - \sqrt{T_c/T_h}$) only a little over two percent efficiency would be possible. Electrochemical cells can operate with relatively high efficiency on hydrogen fuel at body temperature but not using a complex fuel like glucose.

5.2. Control of power generation

Turndown ratio and the rate at which the output power level can be changed are important characteristics of power systems. Increases in energy demands in vertebrate skeletal muscle can range from 40-fold in human muscle to over 400-fold in hummingbird muscle [192]. Relatively short-term increases in cellular energy demands are provided by creatine phosphate (PCr) and by the glycolytic synthesis of ATP [192]. PCr acts as an immediate source of energy (on the order of seconds), whereas glycolysis (anaerobic metabolism) provides

sufficient ATP on the order of seconds to minutes. However, this relatively rapid burst of energy is counterbalanced by the accumulation of metabolic byproducts (e.g. lactic acid) that eventually degrade cellular function. Long term increases in cellular energy demands are met through aerobic metabolism. These changes in cellular energy demand are sensed by the mitochondria, and, given a continuous supply of fuel (sugars, fats) and delivery of oxygen, are sufficiently met by increases in mitochondrial oxidative phosphorylation [185].

In living tissue, the transport of fuels, oxygen, and products occurs initially through the circulatory system and then by diffusion. Larger animals oxygenate through a pulmonary system where oxygen enters the bloodstream and where products are exhausted. In flying insects, high levels of mitochondrial oxygen consumption reflect a mass-specific power input of up to 640 W/kg [193]. Insects achieve this high power density metabolism by diffusing oxygen directly to the cells (see Fig. 24).

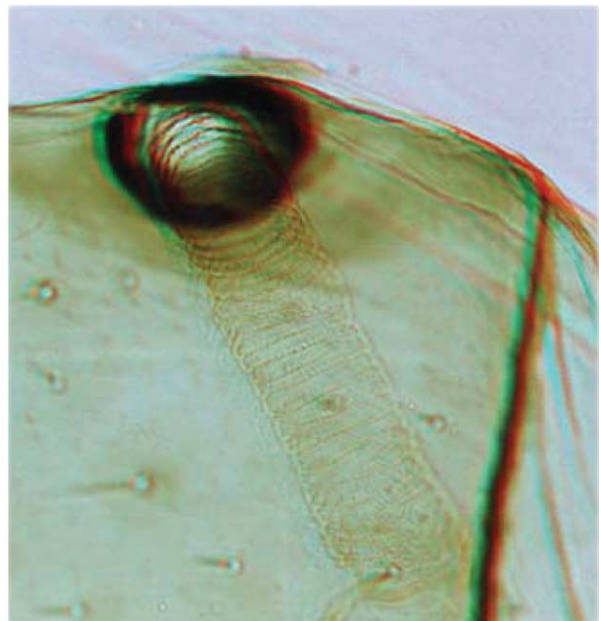
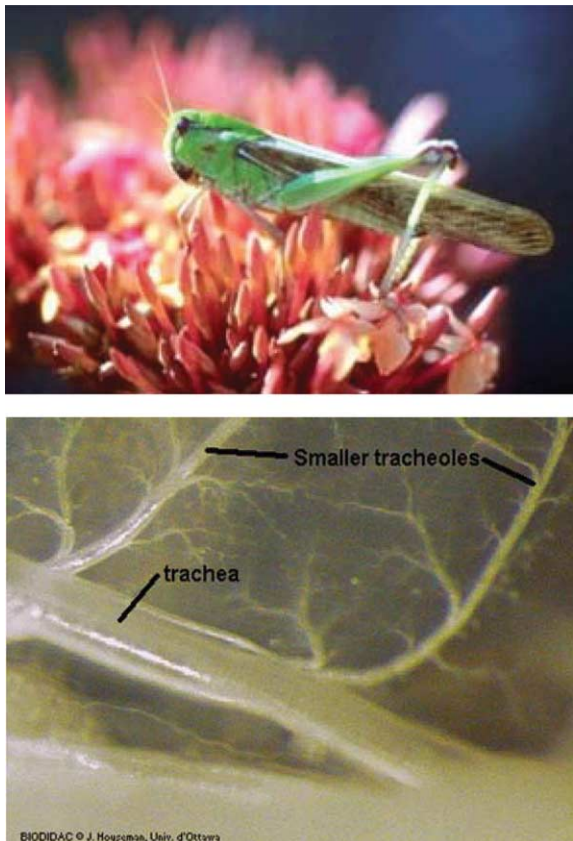


Fig. 24. Insect oxidizer delivery utilizes direct piping of oxygen rather than circulatory mechanisms.

5.3. Power for animal flight

The power density developed by small flying creatures is impressive but to achieve flight they must also make substantial use of natural resonances in their wing structures to minimize the input energy required to maintain wing beats. The fruit fly *Drosophila melanogaster* has been carefully studied by Maughan and Vigoreaux [190] and much work on the dynamics of small flying creatures has been accomplished by Dickinson et al. [194] and Dickinson [195] as well. Hence, a fair amount is known about the mechanics of the flight process. To achieve lift, the fruit fly beats each wing up to 240 times/s over a span of about 170° . Mechanical power is proportional to the cube of both wing beat amplitude and frequency, and the typical power generated, 80 W/kg muscle mass [196], is close to the maximum power available from aerobic metabolism in fast muscle, i.e. about 100 W/kg [197]. Approximately 31 μ W of power is generated by the whole fly. The predicted oscillatory power for individual myosin molecules in *Drosophila* is about 15×10^{-18} W per cross bridge. Hence, to produce the 31 μ W generated during flight, approximately two trillion myosin molecules must work together. As a brief aside, this level of coordinated reaction is enticingly similar to the concept of controlled distributed reaction suggested by Oppenheim and Schock [198] and Oppenheim [199] as the future of combustion in engines. At standard temperature and pressure 1 mm³ of gas contains more than 10^{16} molecules. During coordinated combustion, all of these molecules could be made to react together.

Based on fast camera measurements of the *Drosophila* wing beat amplitude and frequency, mechanical power can be calculated. Carbon dioxide gas analyzers measure energy consumption, from which metabolic power output is determined. The ratio of these is the flight efficiency (ratio of mechanical to metabolic power) and it is approximately 10%, similar to the value reported for other insects [200]. Achieving 80 W/kg muscle mass in *Drosophila* at 10% efficiency, represents 800 W/kg mass specific power input, which is close to the value quoted earlier for hummingbird muscle [193].

Ron Fearing at the University of California, Berkeley [201], has built a flying machine on the scale of a horsefly. Its stainless steel wings are resonant at nearly the same frequency as the living fly, but the power density needed cannot be provided autonomously onboard with any existing power source. The device has been demonstrated only when tethered to a

separate power supply [202]. The challenge of this miniature flying system illustrates how critical power is in achieving the next generation in autonomous devices.

For biological systems, the timescale for action is generally limited by thermal and chemical diffusion rates, particularly in periods of high-energy demand, and this transport limit makes it difficult to achieve high power densities. In addition, because energy conversion is mediated by cell surfaces, the maximum power is controlled by the total available surface area. It appears difficult, therefore, to create an autonomous biologically-derived propulsion engine superior to those occurring naturally that already include full life-support systems.

5.4. Biochemical heat generation

In addition to the increased power demands of the whole organism, the mitochondria within various specialized tissues are capable of very high-energy outputs by regulated changes in mitochondrial respiration. Brown adipose tissue (BAT), for example, has evolved in mammals to generate large amounts of heat for both short-term and long-term regulation of body temperature. The mitochondria that make up this unique tissue have evolved a novel uncoupling protein (UCP1), which mediates a net influx of protons within the mitochondria without ATP production, increasing heat generation [203]. Uncoupling proteins have been found in several isoforms throughout a variety of mammalian tissues. Specialized mitochondrial adaptations for the generation of large amounts of heat occur in non-mammalian vertebrates as well. In 10 species of fish from the family *Scombridae* (includes swordfish and marlins), the extraocular muscles have evolved a heat generation function capable of sustaining energy metabolism estimated up to 250 W/kg [204]. In contrast to BAT, UCPs are not required to initiate the biochemical processes that will uncouple oxidative phosphorylation, but rather use a mechanism termed ‘excitation-thermogenic coupling’ [205]. This specialized mechanism requires the rapid futile cycling of intracellular Ca^{2+} within the skeletal muscle [205]. In the case of BAT and UCPs, the biological system is producing heat rather than chemical currency that can be further converted to work or electrical energy. Though the output in this case is heat, equivalent to what would happen if the glucose were burned directly, the heat release is controlled and can occur at relatively low temperature because the process is catalyzed within

the organism. These are two features that are difficult to obtain in typical thermochemical conversion strategies.

5.5. Summary and conclusions

The relatively high power density potential of mitochondria, along with built-in cellular sensing and regulation functions raise the possibility that such mechanisms can be harnessed as a personal power source, but it will be necessary to have an enhanced understanding of cellular power delivery and its control in order to develop controllable biologically inspired electromechanical power systems. Furthermore, although specific muscle cells have high power density potential, a substantial support (balance of plant) system to provide nutrients, oxygen, fuel, and thermal stability is also necessary. With these added components, it is unlikely that a biological approach will yield a viable solution for personal power that is much more effective than could be achieved from power harvesting directly from the organism itself. In any case, and as noted earlier, achieving biologically-derived or biologically-motivated personal power is virtually unexplored and requires substantial foundation research.

6. Personal power summary and concluding remarks

Delivering personal power in the range of 10–1000 W is a uniquely challenging problem. This scale of power in packages that are portable, quiet, energetic, and capable of long operating duration is too large to use optimally surface reaction approaches (e.g. batteries and fuel cells) and too small to easily control the inefficiencies from heat engines. Nevertheless, this power range is extremely important for autonomous human function. Personal power systems convert the chemical energy stored in fuel into useful work. Such systems represent, by their very nature, transformational technologies that encompass an enormous range of disciplines and their interfaces. For example, the physics of tribology, chemistry of combustion processes and catalysis, chemical engineering of fuel reforming, electrical engineering for power generation and control, materials science for surface protective coatings and fabrication approaches, and mechanical engineering for thermal management, power conversion, and rotating machinery, all play critical parts in the development of power systems. This review only scratches the surface of personal power issues in an

attempt to illustrate how the integration of these fields is necessary to make the next generation power system a reality.

The relative contributions to the overall system performance from the aforementioned research areas are certainly device specific, but one of the greatest hurdles for the successful development of personal power systems currently lies in the balance of plant components required for the successful transition from the laboratory benchtop to the commercial sector of power generation systems, for each of the potential areas: electrochemical, thermochemical and biological. Within the journals of each of these fields, one can find reviews of scholarly works for several of the individual components, including, but not limited to water reclamation systems, fuel reformation, ignition systems, fuel delivery systems, high temperature valving [206], filters, separation technology, cell culture and maintenance, and many more. Where possible, particular examples of these balance of plant issues have been located in the relevant sections to underscore their importance, but an entire review could easily be devoted to addressing balance of plant components.

The need and demand for personal power systems to enhance autonomous human performance is clear, and it would be a pleasure to conclude this review with a concise statement regarding the state-of-the-art in personal power systems, including the insightful reiteration of the seminal breakthroughs, along with a few critical elements that need to be resolved in order to achieve their complete implementation. Unfortunately, small-scale power science and technology has not matured to this level, and the review can instead only identify some important fundamental barriers to resolving the personal power need, as well as some interesting concepts for overcoming these barriers. Consequently, the material can be frustratingly qualitative in nature, and many of the references cited are web-based because much of the work involves device development, and the public outlet for such work is non-traditional. Despite these challenges, however, the review attempts to show how personal power systems of thermochemical, electrochemical, and biochemical nature, as well as hybrid designs among them, all have some future role in addressing the personal power needs suited to their inherent power delivery characteristics.

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